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Ottimizzazione delle condizioni di lavoro del sistema di recupero R134a di CMS per camere a piastre resistive

Optimization of working conditions of CMS's R134a recovery system for resistive plate chambers

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Abstract

R134a is an important gas for the gaseous mixture used to feed the Resistive Plate Chamber (RPC) in CERN's experiment Compact Muon Solenoid (CMS). The mixture has also other components such as water, SF6, nitrogen and isobutane. This last component forms a minimum azeotrope with the R134a (65/35 R134a/isobutane) which makes the R134a's separation and purification particularly difficult. R134a is a Green House Gases (GHG) with a high Global Warming Potential (GWP), its cost is very high not only because of the big volume needed to use the CMS revelator, but also because the European political choice discourages the use of GHG with their taxation. A system to recycle as much as possible R134a is not only an economical choice but also an ethical one. The main component of gas detectors is the gas mixture that must be correct and stable for the proper system's working; the use of expensive and greenhouse gases cannot be avoided because of physical requirements that impose certain choices on the gas mixture composition.

The aim of this thesis consists of a study of the R134a recuperation system working on CMS, with the goals to find the key variables that allow the separation, to optimize them, and finding out if the system can work in continuous or semi-continuous to manage all the gas needed for the CMS working. The separation is based on a distillation process because the composition of the mixture is possible to do a standard distillation eliminating the azeotrope (65/35 R134a/ isobutane) in the vapor phase. Part of the R134a is wasted to allow the formation of the azeotrope and so the purification, but the recuperation efficiency after the purification is around 80%.

The performances of the distillation process were studied and optimized in the light of gas chromatography measurements. The effects of experimental parameters affecting the performance have been investigated.

Considering the experimental evidence reported in this Thesis, the system's semi-continuous operating mode is available and well-tested, and it can trait the needed volume of gas with 80% efficiency and 99.9% of R134a purity. The continuous mode also has been tested, but only superficially and encouraging results were obtained.

Abstract
R134a è un gas importante per la miscela gassosa utilizzata per alimentare la Camera a Piastre Resistive (RPC) nell'esperimento Compact Muon Solenoid (CMS) del CERN. La miscela contiene anche altri componenti come acqua, SF6, azoto e isobutano. Quest'ultimo componente forma un azeotropo di minima con il R134a (65/35 R134a/isobutano), il che rende particolarmente difficile la separazione e la purificazione del R134a. Il R134a è un gas ad effetto serra (GHG) con un elevato potenziale di riscaldamento globale (GWP), il suo costo è molto elevato non solo a causa del grande volume necessario per l'uso del rivelatore CMS, ma anche a causa della scelta politica europea che scoraggia l'uso di GHG con tassazioni. Un sistema per riciclare il più possibile il R134a non è solo una scelta economica, ma anche etica. Il componente principale dei rivelatori di gas è la miscela gassosa, che deve avere una composizione definita e stabile per il corretto funzionamento del sistema; l'uso di gas costosi e ad effetto serra non può essere evitato a causa di requisiti fisici che impongono determinate scelte sulla composizione della miscela gassosa.
Lo scopo di questa tesi consiste nello studio del sistema di recupero del R134a utilizzato nel CMS, con l'obiettivo di individuare le variabili chiave che permettono la separazione, ottimizzarle e verificare se il sistema può funzionare in modo continuo o semi-continuo per gestire tutto il gas necessario per il funzionamento del CMS. La separazione si basa su un processo di distillazione in quanto la composizione della miscela permette di effettuare una distillazione standard eliminando l'azeotropo (65/35 R134a/isobutano) nella fase di vapore. Parte del R134a viene perso per consentire la formazione dell'azeotropo e quindi la purificazione, ma l'efficienza di recupero dopo la purificazione è di circa l'80%.
Le prestazioni del processo di distillazione sono state studiate e ottimizzate alla luce delle misurazioni di cromatografia gassosa. Sono stati esaminati gli effetti dei parametri sperimentali che influenzano le prestazioni.
Considerando le evidenze sperimentali riportate in questa tesi, la modalità di lavoro semi-continua del sistema è disponibile e ben testata, ed è in grado di gestire il volume necessario di gas con un'efficienza dell'80% e una purezza del R134a del 99,9%. La modalità continua è stata anch'essa testata, ma solo superficialmente, e sono stati ottenuti risultati incoraggianti.

RIASSUNTO

Il lavoro di tesi qui presentato è stato svolto presso il CERN (European Organization for Nuclear
Research) di Ginevra nel dipartimento EP-DT-FS (Experimental Physics – Detector Technologies – Fluidic Systems) sotto la supervisione del Dottor Roberto Guida.

Lo scopo di questo lavoro è stato quello di ottimizzare le condizioni di lavoro del sistema di recupero dell'R134a, componente principale della miscela gassosa utilizzata nei rivelatori Resistive Plate Chamber (RPC) dell'esperimento Compact Muon Solenoid (CMS), per ottenerlo nel minor tempo possibili alla maggior purezza possibile.

CMS è uno dei quattro grandi esperimenti situato lungo la circonferenza dell'anello del Large Hydron Collider (LHC, Figura 1), l'acceleratore di particelle più grande e potente fino ad ora realizzato. È costruito in un tunnel sotterraneo con una circonferenza di 27 km, a 100 m di profondità. È un acceleratore di tipo circolare che può accelerare adroni (protoni e ioni pesanti) fino al 99.9999991% della velocità della luce per farli successivamente scontrare con un'energia che, nel centro di massa, raggiunge i 13 TeV, energia vicina al limite teorico dell'acceleratore stesso (14 TeV). La macchina accelera due fasci di particelle che viaggiano in direzioni opposte, ciascuno in un tubo a vuoto. I fasci collidono in quattro punti lungo la circonferenza in corrispondenza di caverne nelle quali il tunnel si allarga per lasciare lo spazio alle sale sperimentali.

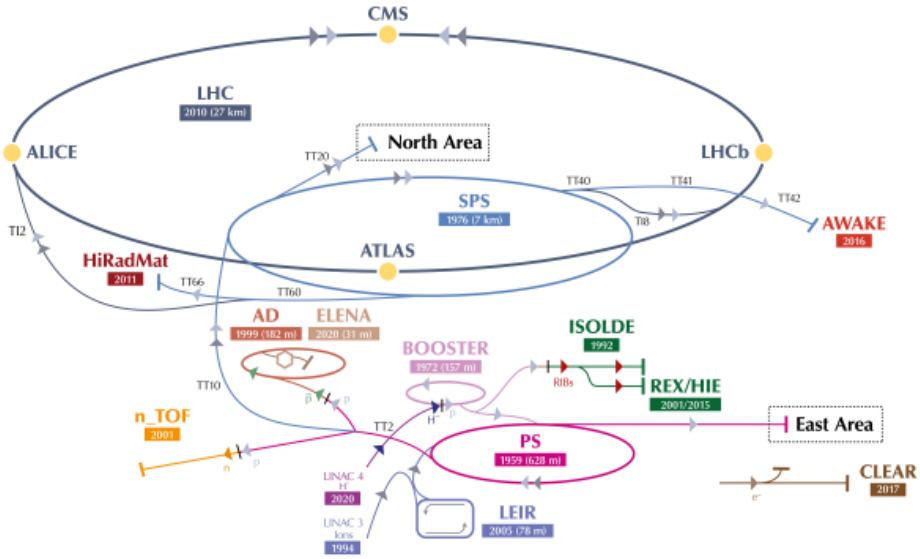

Figura 1 visione schematica del complesso del CERN

Posti lungo la circonferenza dell'anello principale ci sono quattro esperimenti principali che sono rispettivamente ALICE, ATLAS, CMS e LHCb.

Questi esperimenti permettono di fare rilevazioni qualitative e quantitative riguardo ai fenomeni derivanti dalle collisioni dei fasci di particelle. Ognuno di questi esperimenti è composto da una serie di rilevatori. I principali rivelatori (uguali per tutti gli esperimenti) sono:

- Rilevatori interni (Inner Detector): collocati vicino al punto di collisione, permettono di tracciare e misurare il momento delle particelle cariche.
- Calorimetri adronici ed elettromagnetici: misurano l'energia degli adroni, dei fotoni e degli elettroni che attraversano il loro volume, in base all'energia persa dalle particelle che emergono.
- Spettrometro muonico: i muoni sono particelle che non vengono rilevate dai calorimetri adronici, questi rilevatori sono posti nello strato più esterno dell'esperimento, e permette di rilevare la traccia di molti eventi significativi che coinvolgono i muoni stessi. Il gas trattato durante il lavoro di questa tesi proviene proprio da questi detector, posti sull'esperimento CMS.

A cause del gran numero di eventi che avviene ogni secondo (ventidue collisioni ad ogni incrocio, che avvengono ogni venticinque miliardesimi di secondo) si ha un sistema di "trigger" per selezionare solamente gli eventi più significativi, per riuscire a studiare solamente gli eventi significativi per i fenomeni fisici studiati.

Gli RPC, i rivelatori nei quali è impiegata la miscela in esame in questa tesi (da cui è separato l'R134a), sono rivelatori a gas per la rivelazione dei muoni. In generale, un rivelatore a gas è un dispositivo che rivela la presenza di particelle: se una particella che attraversa un gas ha sufficiente energia per ionizzare il gas stesso, vengono prodotto coppie elettrone – ione lungo la traccia della particella stessa. Queste coppie possono essere raccolte e ulteriormente moltiplicate usando un campo elettrico sufficientemente intenso che permette la migrazione degli elettroni verso l'anodo positivo e gli ioni verso il catodo negativo.

Gli RPC sono rivelatori a gas costituiti da due elettrodi piani separati da una camera contenenti una miscela a gas specifica, volta all'ottimizzazione delle performance del detector. I due elettrodi sono posti a potenziale differente, in modo da creare un forte campo elettrico all'interno della camera stessa. Le particelle che, attraversando la camera, ionizzano una molecola di gas, sono rilevate, creando una coppia elettrone – ione (prima ionizzazione). Elettrone e ione vengono accelerati dal campo elettrico e migrano verso anodo e catodo rispettivamente. Tra i due, essendo l'elettrone più leggero subisce una maggiore accelerazione. Durante la migrazione, gli elettroni possono collidere con altre molecole di gas portando alla formazione di altre coppie elettrone – ione (seconda ionizzazione). Elettrone primario e secondario vengono nuovamente accelerati e continuano la migrazione, tramite un processo di moltiplicazione. Gli elettroni devono avere sufficiente energia (in funzione dell'intensità del campo elettrico) per permette la formazione della cosiddetta valanga di elettroni. La diversa velocità di deriva degli ioni rispetto quella degli elettroni (circa un fattore 10^3), la valanga crea una distribuzione di carica (a forma di goccia) che genera un campo elettrico opposto a quello del rivelatore; quando questi due campi elettrici hanno la stessa intensità, la moltiplicazione si arresta: gli ioni e gli elettroni si ricombinano emettendo fotoni (UV) che a loro volta possono ionizzare il gas dando origine ad ulteriori fenomeni di ionizzazione.

Le molecole ionizzate raggiungono l'elettrodo producendo una carica totale abbastanza grande da essere letta da un sistema di lettura costituito da strisce metalliche. Queste strisce vengono colpite in più rivelatori dello spettrometro a muoni in modo da fornire una misura del momento

del muone; questo dato viene utilizzato dal sistema di trigger per definire l'importanza del dato ottenuto in modo tale da ricostruire l'evento a partire dal momento stesso e dall'energia.

La scelta della miscela gassosa di riempimento è cruciale, in quanto le prestazioni e l'efficienza dell'intero detector dipendono da questa. Una miscela gassosa di riempimento deve avere determinate caratteristiche:

- Un basso voltaggio di lavoro
- Un alto guadagno energetico durante il processo
- E una buona proporzionalità, tra numero di particelle rilevate e intensità di segnale.

Vengono usate miscele e non gas puri per migliorare le performance del sistema. I gas di riempimento scelti ovviamente non devono avere caratteristiche per le quali possono costituire in fattore di usura per il rilevatore stesso.
La miscela di gas trattata con il sistema di recupero studiato in questa tesi è composta da:

1. Isobutano 4.5%: utilizzato come quencher di fotoni UV che si formano dalla ricombinazione di ioni e di elettroni durante lo sviluppo delle valanghe di elettroni, cosi da limitare il rumore di fondo dovuto a processi di ionizzazione causati da questi fotoni UV.
2. R134a 95.3%: grazie al suo contenuto di atomi di fluoro è una molecola elettronegativa con un basso potenziale di ionizzazione, in modo da fornire facilmente gli elettroni necessari per la ionizzazione primaria.
3. SF_6 0.3% : necessario per catturare gli elettroni poco energetici e limitare a livello spaziale le valanghe.

Tutti i rilevatori principali hanno una stessa struttura per distribuire i vari gas necessari per far funzionare tutti i rilevatori a dovere. Questa struttura è suddivisa in tre livelli:

- SG: posta in superficie, comprende le bombole di alimentazione dei gas primari, specifiche per tutte le miscele di gas utilizzate nei rilevatori. I gas vengono poi miscelati nelle proporzioni volute da un modulo mixer attraverso dei regolatori di flusso. In quest'area superficiale sono presenti tutte le componenti che richiedono un accesso immediato.
- US: area di servizio sotterranea, fornisce la prima suddivisione della miscela in più linee (pre-distribuzione)

- UX: caverna sperimentale, responsabile della distribuzione vera e propria all'interno dei rilevatori

Una volta che la miscela gasosa è stata utilizzata all'interno dei rilevatori, viene pompata nuovamente in superficie per essere purificata, e immessa nuovamente nel rilevatore. Non si può immettere solamente miscela di recupero all'interno del rilevatore, ma va immessa anche miscela vergine per garantire le prestazioni del rilevatore.
Grazie al sistema di purificazione dalla miscela viene eliminata l'umidità presente, dell'aria (grazie a un primo modulo di purificazione), e di possibili impurità dovute alla degradazione delle componenti principali della miscela (grazie a un secondo modulo di purificazione).
La miscela in uscita da questo processo di purificazione è monitorata per garantire che le proporzioni dei vari elementi e la loro purezza sia adeguata e poi umidificata, per ottenere un livello di umidità sempre costante all'interno del rilevatore.

Nella figura 2 si può vedere lo schema del software di monitoraggio del sistema di ricircolo dei gas del rilevatore. È anche evidenziato il punto di collegamento del sistema con il sistema di recupero dell'R134a, posto dopo i due moduli di purificazione.

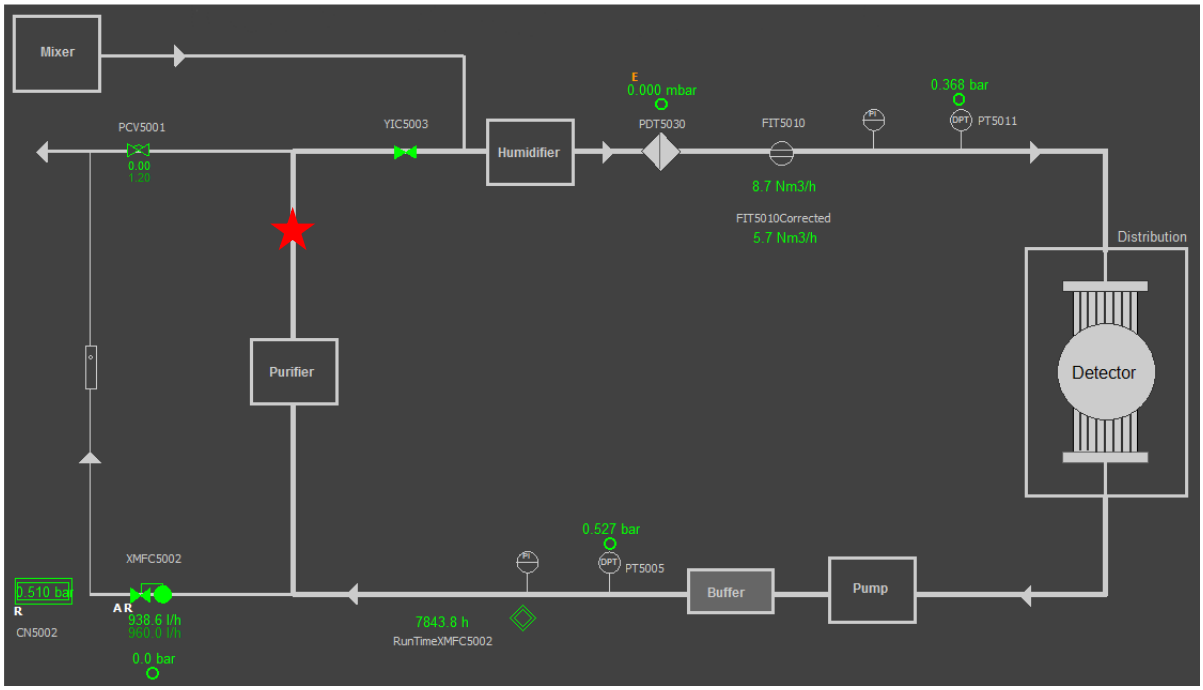

Figura 2 schema del software di gestione del sistema di ricircolo della miscela di gas

Il recupero di questi gas, che sono potenti gas serra, è diventata una necessità, non solamente per motivi ambientali, ma anche per motivi puramente economici. Il prezzo di questi gas e in particolare dell'R134a è molto alto anche a causa di alcune politiche dell'unione europea volte a disincentivare il loro utilizzo. Tali normative sono contenute nel la regolamentazione EU517/2014 e stabiliscono di:

- Limitare di un quinto (rispetto al 2014) il quantitativo totale delle vendite entro il 2030
- Proibire l'uso di gas fluorurati quando sono disponibili alternative meno pericolose;
- Prevenire le emissione tramite controlli, ma soprattutto tramite il recupero (ove possibile).

Per queste ragioni, il gruppo EP-DT-FS del CERN si è reso protagonista di questi cambiamenti necessari, adottando diversi approcci volti alla diminuzione delle emissioni di gas fluorurati. Oltre alla ricerca sperimentale di sostituti validi per i componenti della miscela (dal punto di vista dell'efficienza nei rivelatori), altro approccio importante è quello del recupero dei gas utilizzati nelle miscele stesse: ne sono un esempio il recupero del CF4 (utilizzato nella miscela dei rivelatori CSC) e l'R134a (la cui separazione e recupero sono i focus di questa tesi).

Questo lavoro si focalizza sulla purificazione e il recupero dell'R134a per i motivi sopra citati e per il fatto che sia la componente maggioritaria della miscela di riempimento delle RPC. Cosi anche da ridurre l'impatto ambientale del dovuto al suo utilizzo. Un altro problema che si deve risolvere con questo sistema di recupero sta nel fatto che l'R134a forma un azeotropo di minima con un altro componente della miscela, l'isobutano. L'azeotropo che si forma ha composizione 65/35 R134a/isobutano, in frazione molare. Il diagramma di fase si può vedere nella figura 3

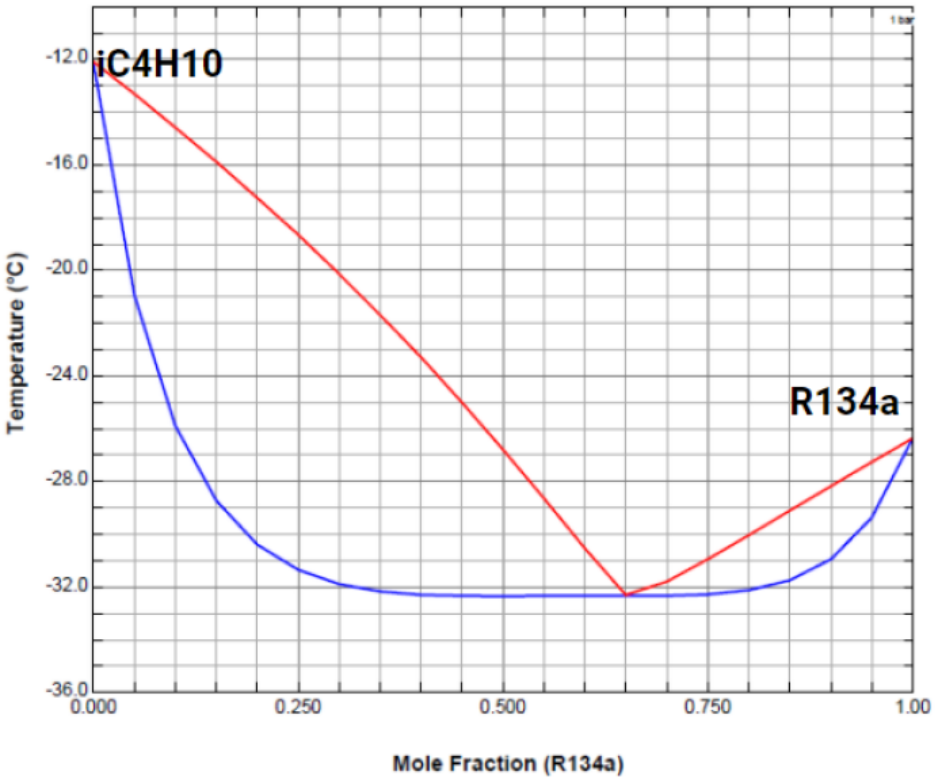

Figura 3 diagramma di fase azeotropo R134a/isobutano

Un azeotropo è una miscela di due o più componenti che non segue un comportamento ideale, e in cui le componenti della miscela hanno delle interazioni tra di loro. In questo modo, come si può vedere dal diagramma di fase (figura 3) si avrà un punto in cui la composizione della fase vapore e della fase liquida avranno stessa composizione e quindi non saranno più separabili con una normale distillazione.

Per poter risolvere l'azeotropo e poter ottenere entrambi i componenti puri si deve ricorrere a dei metodi di distillazione più complessi, o usando diverse colonne a pressioni di lavoro diverse (il punto azeotropico è influenzato dalla pressione) o aggiungendo altri componenti in grado di dividere i componenti che formano l'azeotropo di interesse.

Nel caso preso in considerazione in questo lavoro si ha un azeotropo di minima; quindi, si ha una deviazione positiva dalla legge di Raoult. Il punto azeotropico si trova al di sotto della temperatura di ebollizione di entrambi gli elementi puri che lo compongono. I legami che si istaurano tra A-A e B-B sono più forti di quelli che si istaurano tra A-B.

Visto che vogliamo recuperare R134a puro e che la composizione della miscela di riempimento è 95.2/4.5, la miscela si trova alla destra rispetto al punto azeotropico (figura 3) questo significa che se accettiamo il compromesso di non ottenere una resa di recupero del 100% (ma solamente del'80%) e di sacrificare parte del R134a presente per formare l'azeotropo di minima, si riesce

a ottenere R134a puro nella fase liquida e l'azeotropo nella fase vapore anche con una normale distillazione. Si dovrebbe ricorrere a processi di distillazione più complessi solamente se si vuole recuperare anche l'isobutano. Ma non è questo il caso.
Questo fa si che il set up sperimentale per questo sistema di recupero non sia particolarmente complesso, non richieda l'utilizzo di ulteriori reagenti e possa trattare la quantità di gas necessaria nel tempo necessario senza che sia eccessivamente costoso.

Il sistema di recupero, oggetto di questa tesi, ha il compito di separare R134a da isobutano, e anche da SF_6, l'altra componente maggioritaria della miscela, oltre che da altre possibili impurezze presenti. Lo schema del sistema di recupero in tutte le sue parti si può vedere nella figura 4

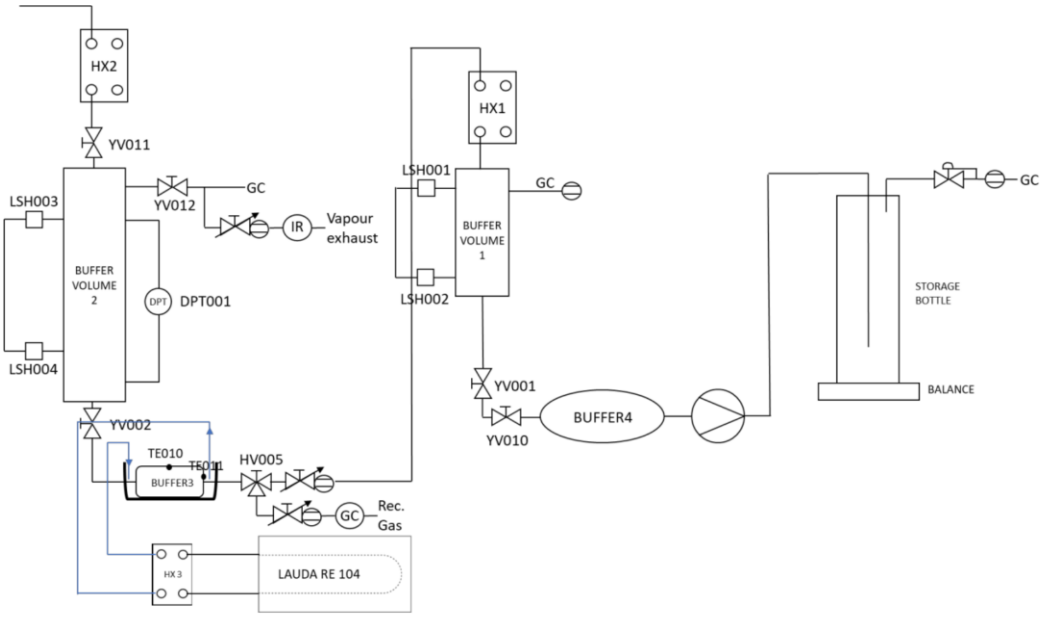

Figura 4 rappresentazione schematica sistema di recupero

La miscela di gas è immessa nel sistema a temperatura ambiente, grazie a una valvola si può decidere se mandare questa miscela all'interno del sistema di recupero o all'exhaust, e nel mentre flussare azoto nel sistema per ripulirlo.
Una volta che la miscela viene immessa nel sistema viene liquefatta una prima volta da uno scambiatore di calore (HX2), a cui segue il primo buffer (buffer 2). La miscela viene raffreddata a -35.5°C, per essere sicuri che tutti i componenti della miscela siano allo stato liquido.

La fase liquida presente nel buffer 2 viene quindi trasferita nel buffer 3, dove avviene la separazione vera e propria. Il buffer 3 è infatti termoregolato a una temperatura di 4.5°C. grazie a questa temperatura nel buffer 3 si accumulerà R134a puro e l'azeotropo (contente isobutano, e l'SF_6) verranno eliminati nella fase vapore attraverso un uscita presente sul buffer2. Dopo un tempo sufficiente per permettere alla separazione di avvenire la fase liquida contenente l'R134a viene trasferita nel buffer1, in cui non avviene alcuna separazione ulteriore in quanto la temperatura è regolata a -35.5°C, da cui poi verrà trasferita prima nel buffer 4 e poi nella bombola di stoccaggio.

Dal punto di vista teorico, avviene prima la separazione dei componenti più volatili (quindi SF6, insieme ad eventuale azoto residuale presente) grazie alla grande differenza di temperatura tra SF6 e il resto della miscela (tetrafluoetano ed isobutano). Successivamente rimangono da separare nella seconda fase R134a e iC4H10; se questi fossero alla concentrazione azeotropica (65/35) non si riuscirebbe a separare queste due componenti tramite semplice distillazione. Tuttavia, essendo la miscela iniziale approssimativamente alla concentrazione 95% R134a/5% iC4H10, la distillazione può avvenire dal momento che ci troviamo lontani dal punto azeotropico; siamo infatti nella parte destra del diagramma di fase. Otteniamo quindi un liquido arricchito di R134a; tuttavia, una parte dell'R134a inizialmente immesso nel sistema andrà perso sottoforma di azeotropo con l'isobutano.

Il sistema di recupero è stato costruito, e inizialmente settato in un lavoro precedente. In tale lavoro sono stati identificati quelli che dovevano essere non sole il migliore setup per il sistema, ma anche le migliori condizioni di lavoro, oltre a dimostrare la fattibilità della separazione con un sistema del genere. Le conclusioni finali di tale lavoro, che costituiscono il punto di partenza per questo lavoro di tesi sono:

- Il flusso di gas in entrata nel sistema non influenza le performances del sistema stesso, è stato testato con flussi in entrata tra 100L/h a 400L/h
- Il modo migliore per controllare la temperatura del buffer 3 è attraverso un bagno di acqua e glicole
- La temperatura di lavoro migliore per il bagno di acqua e glicole è di 4.5°C
- La migliore temperatura per gli scambiatori termici presenti nel sistema è di -35.5°C

Le prestazioni ottenute con queste condizioni operative sono:

- Concentrazione massima di Isobutano: 0.01%
- Concentrazione massima di aria: 20ppm

Una volta appurato che la separazione può effettivamente avvenire con il sistema di recupero costruito, è necessario capire quale sia la quantità di gas massima che è in grado di trattare.

L'obbiettivo della mia tesi è quello di valutare se il sistema di recupero può essere utilizzato per trattare la quantità di gas necessaria al funzionamento degli RPC presenti su CMS, se si può utilizzare in continuo o meno, e quali sono le condizioni migliori del sistema per ottenere questi risultati.

Il lavoro sperimentale è stato suddiviso in fasi:

1. Verifica se il flusso in entrata nel sistema non influenzi le prestazioni del sistema stesso e test di flussi superiori a 400L/h
2. Verifica delle prestazioni del sistema quando lavora in continuo, ma senza compressore per lo stoccaggio
3. Verifica delle prestazioni del sistema quando lavora in continuo, con il compressore per lo stoccaggio
4. Verifica delle prestazioni del sistema in batch con il compressore per lo stoccaggio

(1) Nella prima fase abbiamo testato nuovamente l'influenza del flusso in ingresso di gas sulle prestazioni del sistema, ripartendo da quelle già testate nei lavori precedenti e poi andando a indagare flussi maggiori (fino a 800 L/h). Abbiamo testato il sistema solamente in batch senza fare ulteriori prove in continuo. Durante questa fase inoltre non avevamo a disposizione il compressore a causa di un guasto. Dal test I al test IV è stata usata solamente la prima parte del sistema (il buffer3 è stato collegato direttamente al GC) per verificare il corretto funzionamento del sistema dopo un periodo prolungato di stop.
Dal test 1A al test 5B è stato usato l'intero sistema di recupero. Essendo il buffer2 più grande del buffer1, con il contenuto del buffer2 si riesce a riempire due volte il buffer1.
Con questo prima fase abbiamo appurato che il sistema ha mantenuto le sue funzionalità, e che anche a flussi in entrata maggiori (fino a 800L/h) le prestazioni del sistema rimangono costanti e in linea con quelle ottenute alla fine del lavoro precedente. In particolare non è presente ne

isobutano ne SF_6 e ci sono solamente 10ppm di aria di media. L'efficienza di recupero media è dell'84%.

(2) Nella seconda fase abbiamo fatto funzionare il sistema in continuo, sempre senza compressore che non era ancora disponibile, in quanto uno degli obbiettivi finali è proprio quello di far funzionare il sistema in questa modalità, o quantomeno riuscire a trattare a ciclo continuo tutto il gas necessario. La modalità in continuo consiste nel riempire il buffer2 e una volta pieno aprire tutte le valvole di collegamento con il buffer 3, il buffer 1 e il buffer 4, nel mentre che la miscela percorra tutto il sistema di recupero si continua a immettere nuova miscela nel buffer 2 cosi da mantenere il sistema sempre in funzione, non avere tempi di attesa, e poter trattare una quantità maggiore di gas.
Abbiamo effettuato quattro test, dall' A al D. I risultati sono promettenti, infatti non era presente ne isobutano ne SF_6 , il contenuto di aria è paragonabile a quando il sistema è usato in batch (intorno ai 20ppm) e l'efficienza media è dell' 79%.
Sebbene le prestazioni del sistema in questa modalità siano sufficienti, non avendo a disposizione il compressore la velocità con cui la miscela viene trattata dal sistema di recupero è troppo lenta. Questa fase è servita a capire che il sistema di recupero può potenzialmente lavorare in continuo con le stesse prestazioni di quando lavora in batch.

(3) nella terza fase abbiamo usato il sistema in continuo (con le stesse modalità della fase due) ma con il compressore per stoccare il gas trattato in una bombola. Abbiamo effettuato 6 test, dall' 1c cont al 6c cont. Nei primi tre test non abbiamo controllato il livello di gas presente nel buffer2, ma era libero di variare. I risultati ottenuti in questo modo non erano soddisfacenti; infatti, le analisi hanno mostrato che era presente isobutano, anche se in quantità accettabili (al di sotto dello 0.4%), ma era presente una grande quantità di aria (dal 4% al 9%) e dell'SF_6 (tra i 30ppm e i 70ppm). Essendo presente SF_6 probabilmente il livello di liquido all'interno del buffer2 si abbassava troppo cosi che anche una parte della fase vapore veniva mandata nella bombola di stoccaggio. Per sopperire a questo problema, nei tre test successivi (test dal 4c cont al 6c cont) abbiamo mantenuto il buffer2 pieno per tutta la durata del processo. In questo modo le prestazioni del sistema sono migliorate, e tornate a dei livelli accettabili. In particolare: la concentrazione media di isobutano era del 0.20%, la concentrazione di aria media di 220ppm e l'SF_6 non era presente.
In tutti questi test si può vedere una tendenza generale per il quale all'aumentare del flusso di gas tra le due parti del sistema (tra buffer 3 e buffer1) la concentrazione di isobutano aumenta.

(4) nella quarta e ultima fase abbiamo testato il sistema in batch, ma con il compressore, per verificare se era possibile ottenere concentrazioni migliori di isobutano rispetto alla modalità in continuo.

I primi tre test (test 1c – tets 3c) sono stati eseguiti senza controllare alcun parametro di lavoro, in particoalre il flusso tra le due parti del sistema. In queste condizioni la concentrazione di isobutano media è paragonabile a quella della fase tre. La concentrazione di aria è regolare a attorno ai 250ppm. Le variazioni della concentrazione di isobutano possono essere dovute a causa di un differente velocità di flusso tra le due parti del sistema.

Abbiamo quindi fatto 5 test controllando la velocità di flusso tra le due parti del sistema (test 4c – 8c) ancora una volta possiamo vedere un trend generale in cui all'aumentare della velocità di flusso tra i due buffer aumenta la concentrazione di isobutano presente nella bombola di stoccaggio finale. Durante questa serie di test abbiamo visto che il test 8c mostrava una concentrazione di isobutano insolitamente alta (0.16%) nonostante il flusso tra le due parti del sistema era solo di 100L/h. questo probabilmente era dovuto al fatto che per effettuare quel test abbiamo svuotato troppo il buffer2, e quindi parte della fase vapore sia stata stoccata nella bombola di stoccaggio insieme all'R134a.

Per verificare questa ipotesi, oltre che alla riproducibilità dei risultati ottenuti fino a questo momento, abbiamo effettuato altri 7 test (dal 9c al 16c) controllando, non solo il flusso tra le due parti del sistema, ma anche che il liquido presente nel buffer 2 non andasse mai al di sotto di 20mbar. In questo modo non si sono più riscontrate concentrazioni anomale di qualche componente della miscela di gas a parità di velocità di flusso tra le due parti del sistema.

Infine abbiamo fatto altri sei test in cui abbiamo aumentato la temperatura del bagno di acqua e glicole del buffer3 e da una temperatura di 4.5°C abbiamo impostato una temperatura tra i 9°C e i 10°C. Di questi quattro test sono stati fatti in batch e due in continuo. I risultati ottenuti in questi ultimi test mostrano come la concentrazione di aria non cambia rispetto a tutte le atre prove effettuate (tra i 100ppm e i 300ppm) mentre la concentrazione di isobutano è inferiore (sempre inferiore allo 0.09%). L'efficienza di recupero non diminuisce invece in maniera consistente rispetto alle prove effettuate con una temperatura inferiore del buffer3 (efficienza media del 78%). Questi risultati sono ottenuti indipendentemente dalla velocità di flusso che si ha tra le due parti del sistema di recupero.

Abbiamo quindi visto come il parametro operativo più importante sia la temperatura del buffer 3 e come all'aumentare della velocità di flusso questa debba essere aumentate per far si che ci sia una maggior quantità di calore che possa far avvenire la separazione in minor tempo. Oltre

alla temperatura del buffer 3 altri parametri che possono influenzare le prestazioni del sistema sono: il livello di riempimento del buffer 2 e la velocità di flusso tra le due parti del sistema.
Questo sistema è ancora un prototipo. Un prototipo che è stato dimostrato può effettivamente separare l'R134a dalle altre componenti della miscela, e che può trattare una quantità di gas sufficiente per far funzionare gli RPC solamente con gas recuperato.
Lavori successivi che consistono nella costruzione di un nuovo prototipo devono capire come far funzionare il sistema in continuo oppure come far funzionare il sistema in una sorta di modalità semi-continua con la costruzione di due sistemi di recupero che funzionano in batch e che mentre uno si riempie di miscela gassosa l'altro si svuota per riempire la bombola di stoccaggio e viceversa

Introduction

Large Hadron Collider at CERN

Large hadron collider (LHC) is the largest and most powerful particle accelerator. It is situated at the European Organization for Nuclear Research (CERN) ; it consist in a 27 km ring, 100 m underground, with the aim of accelerating particles beams close to the speed of light, and collide them to study the standard model and to looking for new frontier of physics.

The beam is composed to hadrons, a subatomic particles make of two quarks, most common hadrons are proton and neutron. LHC can work also with heavy ion.

Inside the accelerator two high energy particle beams are made to collide, the beams travel in opposite directions in separate pipes. These pipes are kept at ultrahigh vacuum. Beams are accelerated, focused and deflected in a circular way by superconductive magnets, that need a work temperature of -271.3 °C (1.8K), in this condition magnets can efficiently conduct electricity without resistance or loss of energy. This temperature is obtained with liquid helium, which cools the system. (Anon., s.d.)

The accelerator complex at CERN is a succession of machine that accelerate particles to increasingly higher energy. The source of protons is the linear accelerator 4 (LINAC 4), which accelerate negative hydrogen ions to 160 MeV and injected them to Proton Synchrotron Booster (PSB), the ions lose their electrons during the injection, leaving only protons. The next steps are the injection in the Proton Synchrotron (PS) with an energy of 2 GeV, then in the Super Proton Synchrotron (SPS) with an energy of 26 GeV, and finally in the LHC with an energy of 450 GeV. In the LHC the beams can reach a maximum energy of 6.5 TeV (figure 1). The beams take 20 minutes to reach the maximum energy.

The beams are brought to collision inside four detectors: ALICE, ATLAS, CMS and LHCb. The energy at the collision point is equal to 13TeV.

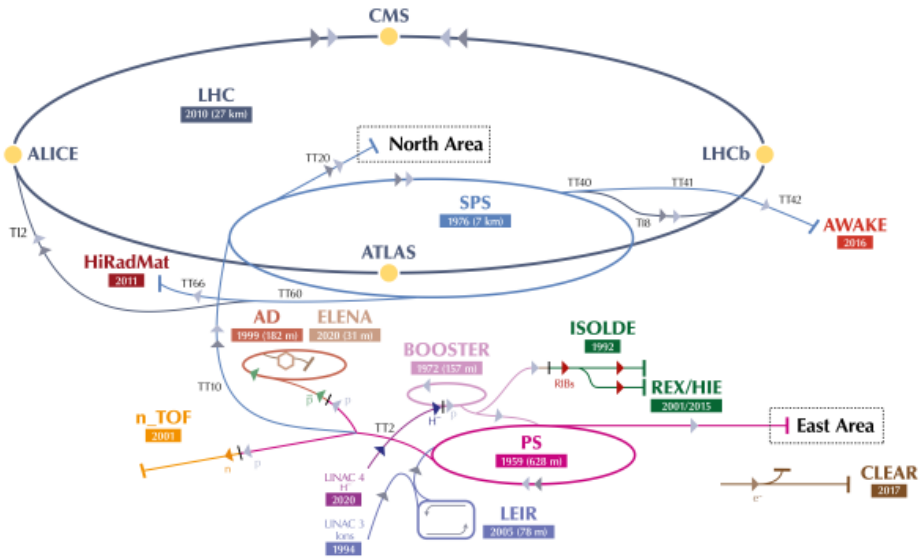

Figure 1: CERN accelerator complex ((Mobs, 2019)

LHC can also accelerate heavy ions, for example vaporize lead can be injected with Linear Accelerator 3 (LINAC3), then injected in the Low Energy Ion Ring (LEIR) and after this follow the same route of the protons (CERN, s.d.)

LHC has eight experiments; the biggest and most important are ATLAS, ALICE, CMS and LHCb. All these four experiments use detectors to analyze the results of the collision. ATLAS (A Toroidal LHC ApparatuS) and CMS (Compact Muon Solenoid) have a general-purpose detectors to investigate the largest range of physics possible, and for searching new particles. The detectors used in these two experiments are different from each other for cross confirmation of new discoveries. ALICE (A Large Ion Collider Experiment) and LHCb (Large Hadron Collider beauty) have detectors specialized for focusing on specific phenomena; ALICE is dedicated to heavy-ion physics. LHCb is dedicated to study the difference between matter and antimatter, in particular studying particles called quark beauty.

The requirements on the detectors composing these four biggest experiments are quite the same, but they work for different final purposes.

These detectors must identify charged particles and measure particles momentum with high resolution. They have three mains different parts:

- Inner detector:

  located close to the collision points, they allow the tracking and momentum measurement of charged particles, as well as vertical reconstruction.

- Hadronic and Electromagnetic Calorimeters :

  They measure the energy of hadrons, photons and electrons crossing their volume, based on the energy loss of emerging particles.

- Muons system :

  Since muons escape the electromagnetic calorimeters, a dedicated Muon system is used to detect them. Typically placed at the outermost layers of the experiments, it allows to unambiguously detect the signature of many relevant events.

Muon Detector Systems

Muons are members of lepton family, with a charge of -1, a mass of 105.6 MeV and a spin of ½. They are the heavy copy of electrons. The only interaction that they have is an electromagnetic one, and they can penetrate and pass undetected the inner detector and the hadronic and electromagnetic calorimeters. Their detection is fundamental for a complete identification and characterization of particles collisions; in fact, they represent a very clear probe for many events of interest. All the most important experiment at CERN have a dedicated detector for the muons identification and tracking.

ALICE (Martinez, 2005)

The ALICE Muon spectrometer is located under the detector. It consists of three absorbers, that need to reduce the initial flux of primary hadrons and protect the detectors from low energy particles created in secondary interactions; a muon magnet, a trigger system; consist of 4 planes of 18 Resistive Plate Chamber (RPC), located between 16 m and 17 m; they operate in avalanche mode, to obtain a high efficient trigger, and a tracking system. (figure 2)

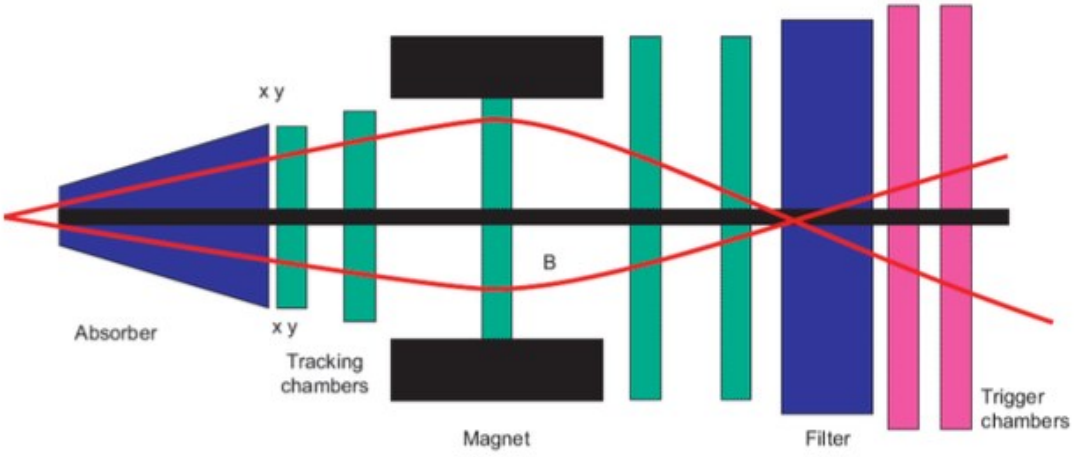

Figure 2 ALICE Muon detector

ATLAS (Efthymiopoulos, 1999)

The ATLAS Muon detector occupied the outermost part of the experiment, it has three large superconducting air-core toroid magnets, one with a barrel form and two placed in the endcaps. This detector has many components the most important are: Monitored Drift Tube (MDT), provide the measurement of the exact momentum, Cathode Strip Chamber (CSC) used in the innermost tracking layer due to their higher capability and time resolution that allow to have optimal performance regardless the high background rate. There are also two types of detectors: the Resistive Plate Chambers (RPC) located in the barrel region, are capable of delivering track information within a few tens of nanoseconds after the passage of the particle, and the Thin Gap Chambers (TGC) located in the endcap region and have the same function of the RPCs.

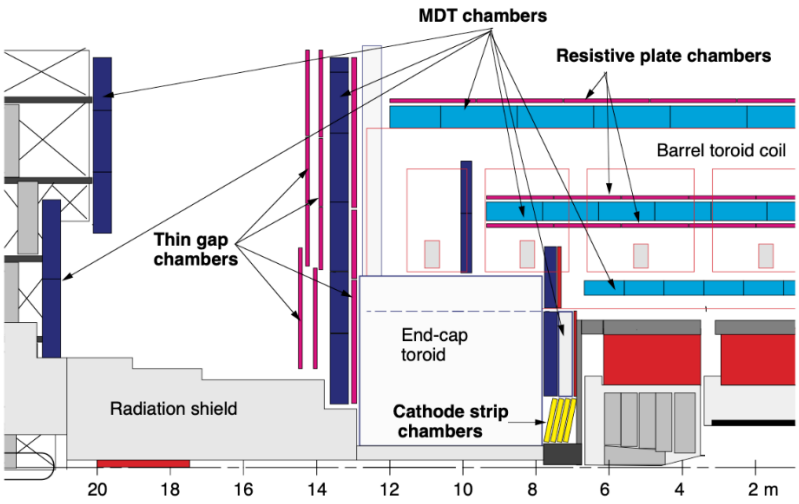

Figure 3 ATLAS muons detector

CMS (Paolucci, 2005)

The CMS experiment structure is based on a super-conducting solenoid, that produces a 4 T magnetic field. The iron yoke is equipped with Muon spectrometer for identification, triggering and momentum measurement.

CMS system is designed to trigger and identify muons; it is based on three different technologies: drift tube (DT), cathode strip chamber (CSC) and resistive plate chambers (RPC). The aim of drift Tube chambers is to measure the spatial position of the muons. They are positioned in four concentric shells in the barrel region of the detector.

RPC are used in both barrel and endcap region as dedicated trigger detectors. That is because of their fast response and good time resolution.

CSC are in the endcaps region and provide precise time and position measurements (figure 4). Because of the many layers of detector and different specialties of each type, the system is able to filter out the background noise.

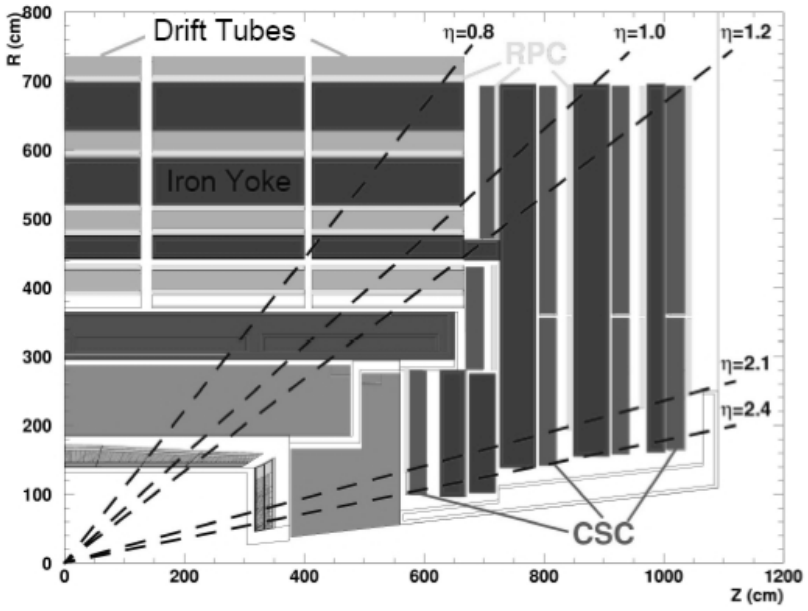

Figure 4 CMS muon soectrometer overview

LHCb (A.A. Alves Jr, 2012)

Muon triggering and offline identification are fundamental aims of the LHCb experiment; that because muons are present in the final stages of many CP-sensitive B meson decay.

The muon system is composed of five detector stations (M1-M5) with a total area of 435 m^2 , with a total of 1380 chambers. The station is placed along the beam axis. Each station is equipped with 276 Multi Wire Proportional Chambers (MWPCs), with the exception of the

inner part of the first station, which is equipped with 12 GEM detectors. Each station is composed by two mechanical independent halves, that can be horizontally moved to access the beam pipe. Stations M2 and M5 are placed downstream the calorimeters and used to identify and trace penetrating muons in both offline and online analysis. Each station is divided into four regions (R1-R4) with an increasing distance from the beam axis. (figure 5)

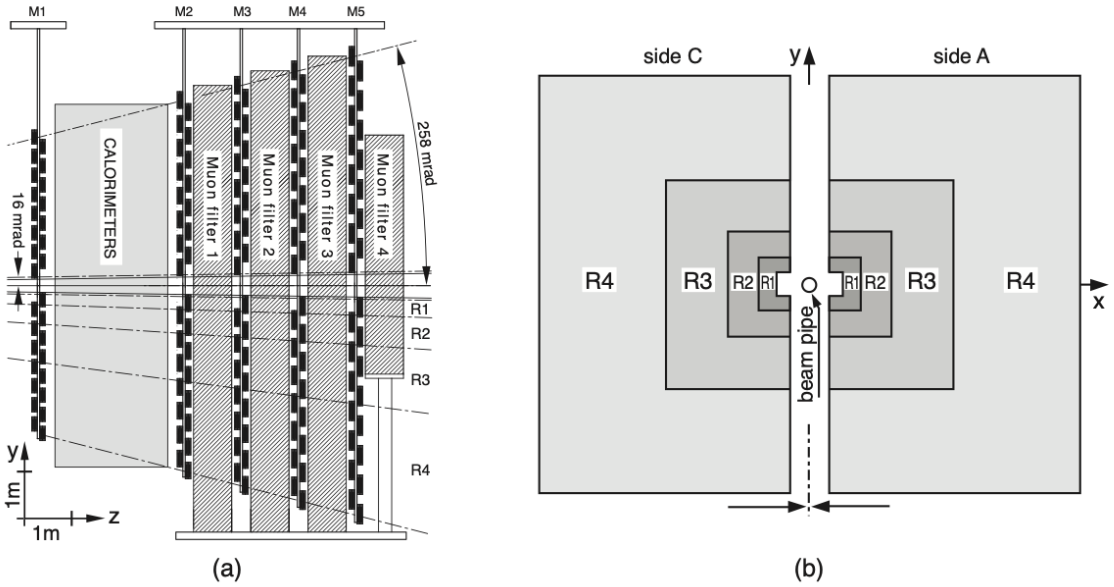

Figure 5 LHCb muon system overview

Gaseous detectors

Gaseous detectors are one of the main components of the Muon detector system. That is because they are capable of precise muon detection. Also, the cost of this kind of detector is affordable; a fundamental point because the large area that this detector must cover.
Muons are the heavy copy of electrons, and they can ionize the filling gas of these detectors. Above this principle the detectors are built.

Gas ionization principle

A fast charged particle passed through a gas can create ionized molecules; a ion pair composed by positive ion and an electron. The schematic reaction of the X species' excitation is:

$$X + p \rightarrow X^{*} + p$$

Where p is a charged particle. A molecule can be excited in many ways, which increase with the increase of the complexity of the molecule. A single atom can be excited only through

photon absorption or emission, a complex molecule can be excited with radiation less transition of rotational and vibrational nature. (Sauli, 2014)
A ionization process can be described in the following way:

$$X + p \rightarrow X^{*} + p + e^{-}$$

The energy of the charged particle must be higher than the ionization potential of the X specie. In this way a ion pair is formed. If the new particles have enough energy they can produce another ion pair, this is called secondary ionization. The total ionization energy will be the sum of the primary and the secondary ionization. The electrons that are formed in this way are detected and generate the readout signal of the detector. All the processes that permits the recombination of the electrons and the process of electron attachment must be avoided, because they do not permit a correct measurement of the detector.

- Electrons recombination process:

$$X^{+} + e^{-} \rightarrow X$$

This phenomenon is caused by electronic attractions. The positive ion and the electron bind themselves again together.

- Electrons attachment process:

$$X + e^{-} \rightarrow X^{-} + \gamma$$

X is an electronegative species that can capture an electron. The result is a negative ion and an energy liberation. Electronegative species that can be present in the mixture are O_2, H_2O, SF_6. These two phenomena can be mitigated with the application of an electric field that favors the mobility and collection. The electric field can also produce the phenomena of electron avalanche that increase the signal. (G. Steinhauser, 2012)

Gas multiplication

If the applied electric field has enough intensity, it can produce the effect of gas multiplication. Free electrons are accelerated by the electric field and gained kinetic energy. If this kinetic energy is higher than the ionization energy of the filling gas molecules, the gas will be ionized, and another ion pair will be produced. Also, the new electrons produced in this way will be accelerated by the field and added ionization phenomena will created. The gas multiplication

process takes the form of a cascade, the Townsend avalanche. In this way the amount of secondary ionization is increased of a factor of many thousand.

Gas ionization and electron multiplication are the gaseous detector's basic principles. The simplest gaseous detector consists of a volume in an enclosure that is constructed to permit a continues flow of gas. The designs of these detectors are many. The most basics is composed by a cylindrical structure with a central wire (figure 6)

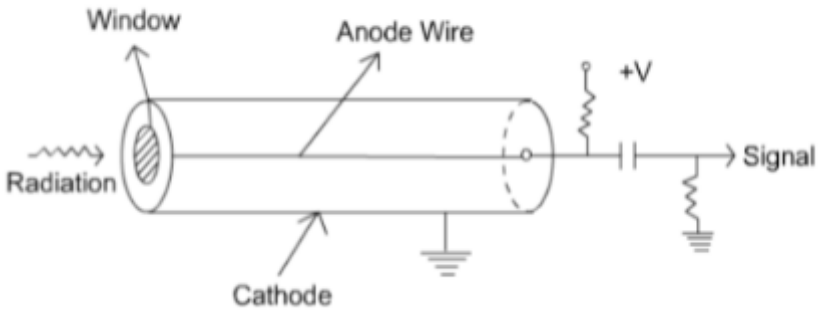

Figure 6 gaseous detector

The wire is the anode, and the outer wall is the cathode. An electric field can be applied across the electrode; the positive ions migrate to the cathode, while the electrons migrate to the anode. When the electrons and ions arrive at the electrode they are collected. The source of the signal is not the collection of the charge particles at the electrode, but the drift of these particles. (G. Steinhauser, 2012)

The parameters of the gas that influence the ionization detector performance are:

- Ionization potential (eV)
- Energy loss is needed to produce an electron ion pair (eV). Part of the energy is lost to excite the medium. Noble gases are preferred due to the absence of vibration and rotation states.
- Number of primary electrons reduced by:
  - Recombination
  - Electrons attachment

Different voltages of the applied field can produce different effects in the gas multiplication. So the voltage determinate the operation mode of the gaseous detector (figure 7):

- Ionization zone: the voltage of the field allows full collection of the charges, but without the amplification (there are no secondary ionizations). The electric field do not accelerate enough the primary electrons.
- Proportional zone: the voltage of the field is strong enough to accelerate the electrons. These electrons can hit the molecules of the filling gas and produce secondary electrons, also the secondary electrons are accelerated and so on, in a cascade process called avalanche. The current is amplified proportionally, and the number of electron-ion pairs in the avalanches is directly proportional to the number of primary electrons.
- Limited proportional zone and Geiger-Muller zone: Increasing further the voltage the ionisation became so high to cause a charge that distorts the electric field which lose proportionality. If the voltage is increased even more the energy become so high that the ions discharges emitting photons. These photons have enough energy to ionise other molecules of the filling gas causing the formation of secondary avalanche that take place along the anode. The output current is no more dependent by the energy of the phenomenon that has caused the first ionisation, because the saturation of the current itself caused by this secondary avalanche. To stop the ions discharge it must be present a quenching gas in the filling mixture which is capable of absorb the photons before that they cause the secondary avalanche.

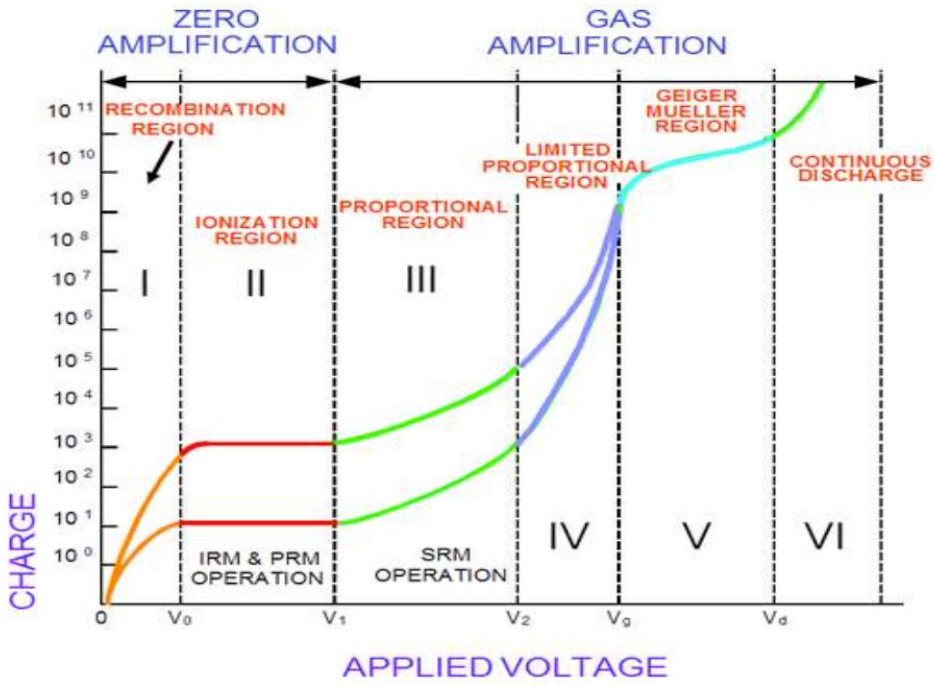

Figure 7 relationship between the pulse size produced and the potential applied across the electrodes.

Filling gas

The choice of the filling gas is very important, that because it influences the gaseous detector's performance and work condition. A good filling gas must have the following characteristics: low working voltage, high gain, good proportionality. To obtain better characteristics is possible to use a mixture of gas and not a pure gas. Usually, noble gases are a good choice because they need a low voltage to obtain avalanche's formation; argon is the most used to its lower cost and higher ionization. The argon alone as filling gas is not convenient, because it reach too high gain level, so is possible to add some quenching gas as CO_2 and i-C_4H_{10} . These molecules can absorb the photons emitted by excited argon atoms and dissipating it with a non-radiative phenomenon, avoiding the formation of too intense avalanche. The signal will still be in the proportional zone. Different type of gaseous detectors requests a different filling mixture. The purity of the filling gas must be constant during the analysis; this aim is obtained with a continuous flow through the chamber. It can be a once-through or a recirculation type. In the first the gas mixture is always new. In the latter the gas mixture after passing through the detector is collected, purified, and then immitted again in the mixture flow. The purification process is fundamental to avoid the presence of undesired molecules that can kidnap electrons or cause more avalanches. (Corbetta, 2018)

Muon detector gas systems

The gas mixture is an important element for this type of detector, a correct and stable mixture composition is needed for a good and stable long-term performance. The basic function of the gas system is to mix the different gas components in the right proportion and deliver them to the corresponding detectors. The LHC gas system has been implemented following a modular design, so it is possible to adapt each detector system maintaining a basic common structure to optimize the building, commissioning and maintenance operations. There are three different levels for the location of the system modules: the surface room (SG), the underground service room (US) and the experimental cavern (UX) (figure 8).

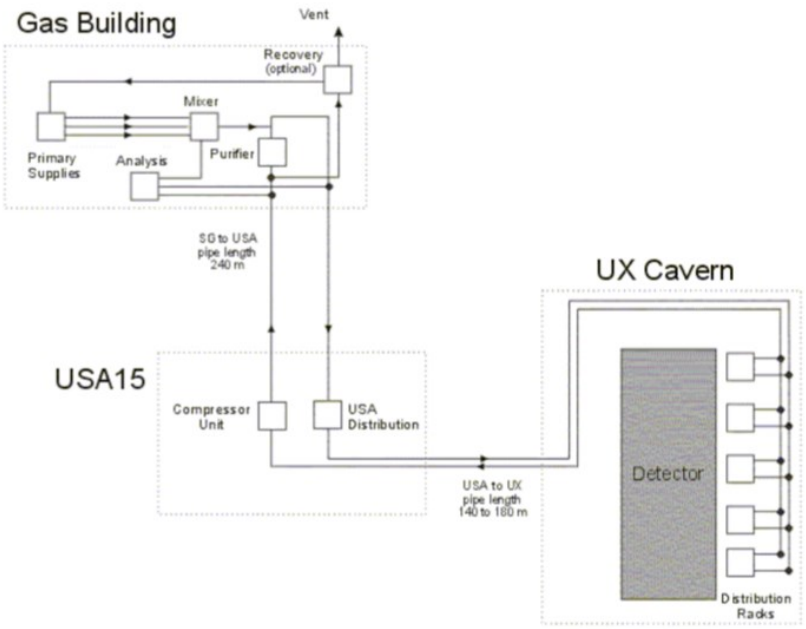

Figure 8 basic module of a gas system

All the units that need an immediate access are located in the SG, together with the primary gas supply. In the US there are gas pre-distribution into several channels and part of the gas system parameters regulation. In the UX there is the effective detailed distribution to each detector. The main components of the gas system are briefly described in the following list:

- Primary gas supply: each gas is provided by two independent supply sources, one in use and one on stand-by. This second source can be used when there is a problem in the primary sources, and when the primary source must be changed.
- Mixer module: primary gases are used to prepare the gas mixture for the detectors. The mixer module has different input lines, equipped with mass flow controllers (MFCs),

that have the aim to control the flux of the primary supplies, and mixing them in the right proportion. The gas mixture is prepared with high precision; with less than 0.1% uncertainty on the concentration value of each gas component. There also is a mixing volume to allow the gas components to mix properly before it is sent to the following module.

- Gas distribution: several steps are needed to distribute the gas mixture to each detector. Pre-distribution modules are located in the US, and they are related to different detector sectors of the experiment. The gas is sent from the US to the UX, where the final distribution modules are located. Each pre-line is split into several smaller lines, to distribute the gas with the required granularity.
- Pump module: once the gas has flown from the UX into the return module the pump module compresses the gas to send it back to the surface. Usually, more pumps are present in a single module to have a back-up pump in case of needed.
- Exhaust module: the gas returning to the surface modules can either be fully exhausted to the atmosphere or sent back to recirculation. The return gas passes through the exhaust module, where volume flow and pressure regulation allow to manage the gas emission in relation to the gas system parameters which are subject to specific requirements.
- Purifier module: this module allows to eliminate some impurities when the return gas is re-injected in the system. The impurities can be accumulated along the gas path, in the gas system elements, or directly in the detectors volume. These impurities can react with the molecules of the gas mixture or can have a negative or positive effect on the experimental signal, avoiding or promoting the formation of new avalanches. The most common impurities are: N_2, O_2, H_2O
- Gas analysis module: it is used to monitor the composition and the quality of the gas mixtures in some critical points (after mixer, exhaust, after purifier). O_2, H_2O and infra-red analyzer are always present; in some case there is also a system to perform a Gas Chromatograph analysis on selected lines to have more accurate and complete measurements.

Fluid mixture separation

Fluid mixture separation process has become an important technique in many industrial fields and application. Distillation is the principal separation method in the chemical and petroleum industries, and it is also amply used in other fields. Distillation is a thermal separation method for separating mixtures in their pure components; this method exploits the different volatility of the components. The volatility is related to their boiling points. So, it is possible adding or remove heat to separate them. The most common industrial uses of the distillation process are separation of crude oil into fractions, water purification and desalination, distillation of fermented solutions.

A distillation method can separate chemical components only if the compositions of the vapor and liquid phase at the equilibrium are different.

Important concept for understanding distillation

Distillation is based on the different composition of the liquid and vapor phase in equilibrium of a mixture with different components. The vapor phase will be richer with the lower boiling point component, and the liquid will be richer with the higher boiling point component. Collecting the vapor phase and condensing it is possible to obtain two different solutions with the different components of the initial mixture pure. (Kiss, 2013)

Vapor pressure:

Vapor pressure is the pressure that pure component exerts at a given temperature when both liquid and vapor phase are present. Vapor pressure is related to boiling, and it increase with the energy input; when a liquid boils his vapor pressure is equal to the ambient pressure. A liquid with a high vapor pressure boils at a low temperature and vice versa. The vapor pressure of a liquid mixture depends on the relative amounts of the components in the mixture. The vapor pressure of an ideal mixture is described by the Raoult's law (figure 9):

$$p = \sum_{j=1}^{Nc} p_j = \sum_{j=1}^{Nc} p_j^* \chi_j$$

Where p is the vapor pressure of the mixture, p_j^* is the vapor pressure of the pure component, and χ_j is the molar fraction of the component j. The consequence is that the partial pressure of the single component of the mixture is:

$$p_j = p_j^* \chi_j$$

This equation is valid only in equilibrium state between the vapor and liquid phase, and only for ideal solutions. The vapor pressure depends only on temperature if the component is pure. If the component is in a mixture the partial pressure depends also on the molar fraction. The higher the vapor pressure of the pure component higher the volatility of the component itself. Increasing the temperature, the partial pressure increases exponentially. The dependence of the vapor pressure on the temperature is a strong one. With this law is possible to build the temperature composition diagram; a type of phase diagram where the boundaries show the composition of the phases that are in equilibrium at various temperature (at a given pressure). (Kiss, 2013)

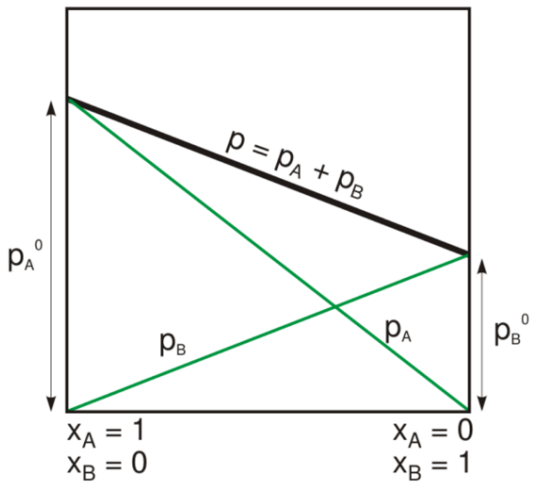

Figure 9 Roult's law representation for a binary mixture

Vapor-liquid equilibrium:

It is represented by a T-xy diagram (figure 10), where T is the temperature, and x and y are the vapor and liquid molar fraction of one component of the mixture. The pressure is constant. It is very useful as representation because in the distillation process, usually, the pressure doesn't change.

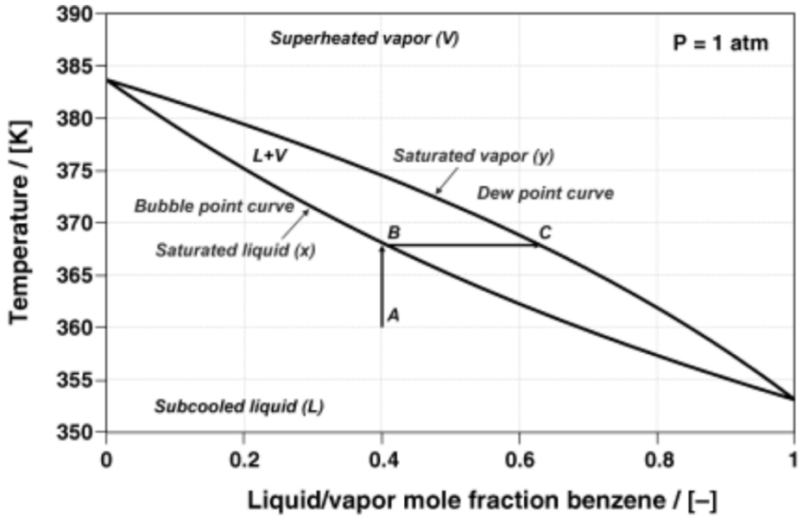

Figure 10 example of T-xy diagram

In figure 10 is represented the T-xy diagram of a mixture of benzene toluene. The temperature corresponding to a molar fraction of 1 of the benzene is the boiling point of the benzene. Where the molar fraction of the benzene is 0, the corresponding temperature is the boiling point of pure toluene. The lower curve in this diagram is the bubble-point curve, the upper curve is the dew-point curve. The bubble point curve gives the mole fraction of benzene present in the liquid phase at a certain temperature, while the dew-point curve gives the mole fraction of the benzene in the vapor phase. Drawing a horizontal line at a certain temperature and reading off his intersection with the two curves gives the composition of the liquid and vapor phase. The liquid and vapor phases are present in equilibrium when the point considered is between the two curves. The difference between vapor and liquid phase composition makes it possible use this technique to separate the mixture's component. (Kiss, 2013)

Relative volatility:

It is a measure of the differences in volatility between two components. It is important to estimate if two components of a mixture can be separated with a distillation, and how easy or difficult will be. A simple rule is that the larger the relative volatility, the easier the separation through distillation. The formula to estimate the relative volatility is:

$$\alpha_{LH} = \frac{y_L / x_L}{y_H / x_H}$$

Where L is the light component and H is the heavy component; y is the vapor mole fraction, and x is the liquid mole fraction. This formula estimates the relative volatility of the component L respect to the component H. it can be used not only for binary mixtures, but also for multicomponent mixtures with the right adjustment.

In a binary system it can be used to give a simple relationship between the component in the liquid and vapor phase, with x and y being the mole fraction of the light component in the liquid and vapor phase.

If there is a multicomponent mixture with a constant relative volatility is possible to find a relationship between vapor and liquid composition analogue to the one for the binary systems:

$$y_j = \frac{\alpha_j x_j}{\sum_{j=1}^{Nc} \alpha_j x_j}$$

The lightest component of the mixture is component 1, the second lightest is the component 2 and so on until the heaviest component of the mixture; y is the vapor mole fraction and x is the liquid mole fraction. This equation is valid only for a mixture where the components have a constant relative volatility (Kiss, 2013).

The relative volatility changes with temperature, pressure, and composition. If two components have the relative volatility equal to 1 they form and azeotrope, and they can never be separated into pure components by ordinary distillation.

Distillation process

When a liquid of composition a_1 is heated, it boils when the temperature T_2 is reached (figure 11). So the liquid has a composition a_2 and the vapor has composition a_2^I. The vapor is richer in the more volatile component A, and as consequence the liquid is richer in the less volatile component. In a simple distillation the vapor is collected and condensed, and it is used to separate volatile components from non-volatile solute.

The vapor of composition a_2^I can be condensate to form a liquid of composition a_3. This liquid has a boiling point temperature of T_3, so it can be distilled again in the same way as before. At a temperature of T_3 the liquid phase has a composition of a_3 and the vapor phase has a composition of a_3^I. This loop can be repeated again and again until the pure components are obtained. When a distillation has more than one step is called fractionated distillation, and it is used to separate volatile liquid. The cycle's number of vaporisation-condensation which are

needed to obtain a condensate with a specific composition from a given distillate is an indicator for the efficiency of the fractionating column. This number is called theoretical plates (Paula, 2017)

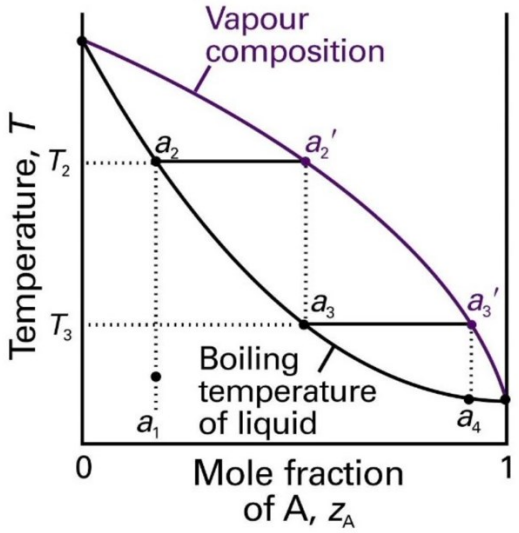

Figure 11 temperature composition diagram for an ideal solution. The component A is the more volatile of the mixture. The component B is less volatile (Paula, 2017).

Azeotrope

It is a mixture where its components interact with each other, in that case the behavior is not ideal, and the temperature-composition diagram change from the classic one (figure 12).

An azeotrope is a liquid mixture that has a maximum or minimum boiling point temperature that is lower or higher than that of any other component of the mixture. Its boiling point temperature is lower or higher dependently of the molecular interaction. The molecules of the different mixture's component interact with each other, and that provoke that the Raoult's law is no more respected.

Imagine having a mixture of two component A and B, if the two components interact with each other their behavior will be not ideal. A non-ideal behavior generates a temperature-composition diagram which has a maximum or minimum (depends on if the A-B interaction is stronger or weaker than the A-A and B-B interactions) in this maximum/minimum point the composition of the liquid phase will be the same of the vapor phase, so a normal distillation cannot separate the two component.

If the interaction A-B is stronger than the interaction A-A and B-B; the A-B interaction stabilize the mixture, and the excess Gibs energy (G^E) will be negative, with the consequences that the two components are more favorable to mixing than a ideal mixture; a maximum azeotrope is formed. And the azeotrope boiling point will be higher than the boiling point of the two separate components (figure 12a). If the interaction A-B is weaker than the interaction A-A and B-B; the A-B interaction destabilizes the mixture, the G^E will be positive, the two components will be less favorable to mixing than a ideal mixture; a minimum azeotrope is formed. In that case the azeotrope boiling point will be lower than the boiling points of the two components of the mixture (figure 12b).

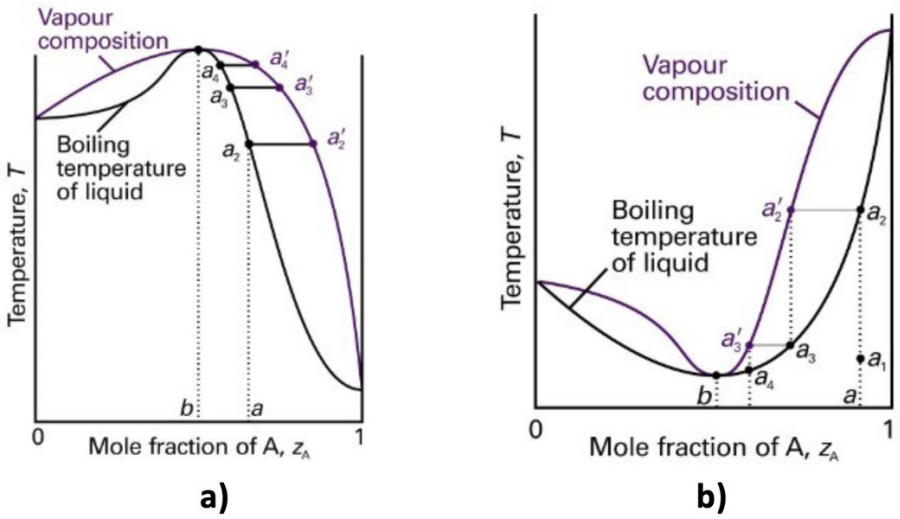

Figure 12 temperature-composition diagram to high-boiling azeotrope (a) and low-boiling azeotrope (b) (Paula, 2017)

The tendency of a mixture to form an azeotrope depends on two factors: the degree of non-ideality (the activity coefficient) and the difference in the pure components boiling points. The closer the boiling points and the lesser the ideal mixture, the greater the likelihood to form an azeotrope. (Hilmen, 2000)

An azeotropic mixture can't be separated with a normal distillation or a fractionated distillation. In a distillation if is present a maximum azeotrope, liquid phase will tend to achieve the azeotropic point, while the vapor phase will be collected as one of the two pure components of the mixture, dependently of the lobe of the temperature-composition diagram where the initial composition of the mixture is posed. So, when the liquid phase achieves the azeotropic point, the liquid and vapor phase will have the same composition and the distillation must be stopped.

If there is a minimum azeotrope, will be the vapor phase to tend to the azeotropic point, and the liquid phase will contain one of the pure components of the mixture dependently to the initial composition of the mixture. The vapor phase with the azeotropic composition is not possible to divided in a conventional way. This phase condensed has the same composition of the vapor phase. The distillation must be stopped.

Deviation from ideal behavior

Vapor-liquid phase equilibrium for a multicomponent mixture can be expressed, when the pressure and temperature are lower than the critical point or moderate away from it, as:

$$y_i P = x_i \gamma_i(T, x) P_i^{sat}(T)$$

Where y_i and x_i are the vapor and liquid composition of component i. P is the pressure of the system, T is the temperature, γ_i is the activity coefficient of component i in the liquid phase, P_i^{sat} is the saturated vapor pressure of component i. γ_i is a good measure of the ideality or non-ideality of a mixture. If γ_i = 1 the equation can be simplified to obtain the Raoult's law. The activity coefficient changes with the changes of composition and temperature.

When the activity coefficient is different from 1 the mixture is not ideal, and the Raoult's law is not respected. If γ_i < 1 the deviation from the ideality is negative (it is a maximum-boiling azeotrope); if γ_i>1 the deviation is positive (it is a minimum boiling azeotrope). When the deviation from ideality is large, the temperature-composition diagram shows extreme point (positive or negative dependently by the negative or positive deviation from ideality). This extreme point is the azeotropic point. An azeotropic mixture is formed.

The azeotropic point can change dependently by the temperature and/or pressure of the system. In the azeotropic point the composition of the liquid and vapor phase are the same (x = y). The condensation and boiling temperature curves are tangential with zero slope (Hilmen, 2000).

Multicomponent mixture

Multicomponent mixture and in particular ternary mixture can form an azeotrope. In such case, the normal temperature-composition diagram is no longer useful. The azeotropic point can be not in extreme position but in some other, int that case the diagram has a saddle. This type of mixture is called saddle azeotrope, their representation is shown in figure 13

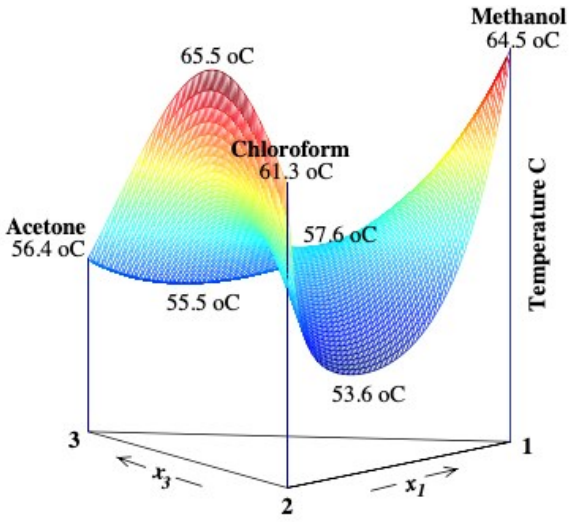

Figure 13 representation of a saddle azeotrope formed by chloroform, methanol and acetone (Hilmen, 2000)

Other representation of a ternary azeotropic mixture is a triangular one (figure 14) (Hilmen, 2000).

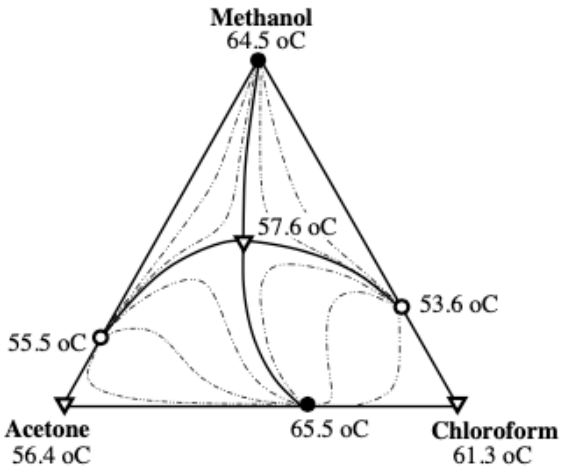

Figure 14 residue curve map for mixture in figure 14. the residue curves' singular points are indicated by ■ (stable node), O (unstable node), ∇ (saddle), and boundaries by bold lines. (Hilmen, 2000)

How to resolve an azeotrope

There are different ways to resolve an azeotrope and separate the different components of the mixture. It is possible to distinguish three different main categories: enhanced distillation, membrane process, process intensification (figure 15).

All these three main categories have the aim of breaking the azeotrope and make the separation possible. This aim is reached by modifying the operative condition to surpass the azeotropic point. Usually is used a third element, called entrainer, or the characteristic of the membrane, or change the pressure or temperature of the distillation. Also, the intensification of the distillation process with microwaves or ultrasonic is possible. A classic distillation is useless with this type of mixture if the goal is to obtain both the components of the binary mixture pure.

Enhanced distillation

There are two main strategies for an enhanced distillation. The first one is adding a third component to the azeotropic mixture (called entrainer). This component is able to change the relative volatility of the two components of the azeotrope, so to make possible the separation with a distillation. The second one is to work with two distillation columns with different pressure each. The azeotropic point can change with the changing of the operative pressure. This technique is called pressure swing distillation.

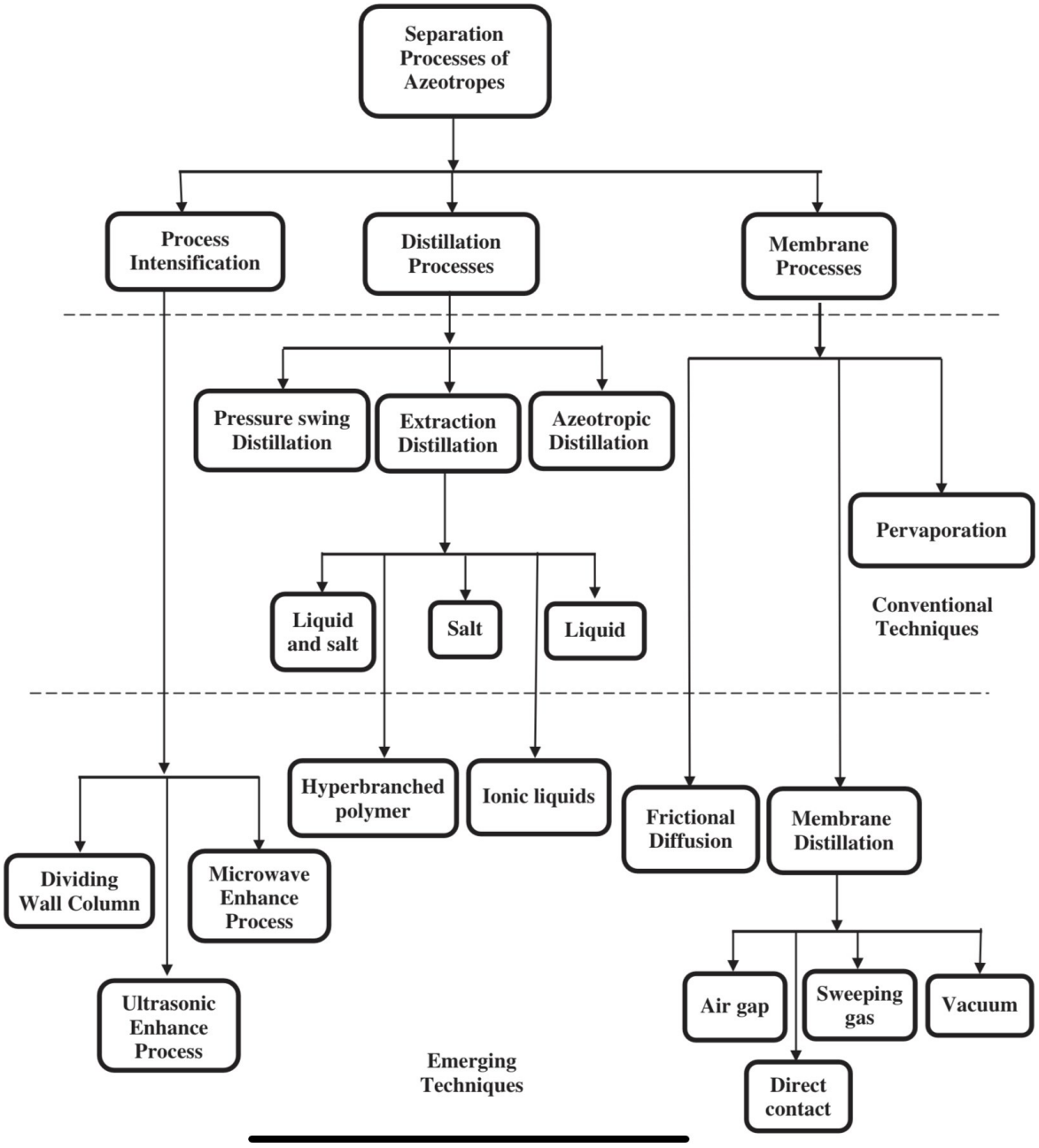

Figure 15 schematic diagram of various technique for separation of azeotropic mixtures. (T. Mahdi, 2014)

Distillation using an entrainer:

The principal technique which uses an entrainer are azeotropic and extractive distillation; both have the same experimental set up (or really similar each other; the nature of the entrainer can gently change it). The set up consists in two distillation columns. One of the columns needs to separate one component of the mixture to the second component and to the entrainer, the second columns need to separate the entrainer and the second component of the mixture. The entrainer needs to increase relative volatility of the two components, and in particular to change the activity coefficient of the different component of the mixtures.

The entrainer is a kay element for these separation process, and it must be chosen accurately dependently to the original mixture's components. For these goals it is selected considering the way it influences the *selectivity*; the selectivity is the ratio between the activity coefficient of the two components of the mixture:

$$S_{ij} = \left(\frac{\gamma_i}{\gamma_j}\right)$$

Where S_{ij} is the selectivity, γ_i is the activity coefficient of component i, and γ_j is the activity coefficient of the component j. More the value of S_{ij} differs from 1 better the separation can be accomplished. Also, the entrainer's cost can influence the choice. The selectivity is the only variable that influence the relative volatility when the pure components' vapor pressure does not change significantly at the changing of the temperature.
The entrainer must also have a boiling point temperature significantly different from the other component to facilitate the separation and recovery in the second column.

Azeotropic distillation:
In this process is used an entrainer which form an azeotrope with the highly volatile component. Only a relatively small part of the entrainer forms the azeotrope. The entrainer and the highest volatile component are taken off from the top of the first column and used as feed for the second column. In this second column the entrainer is taken off from the top of the second column and sand back to the first column to form again the azeotrope. The pure components are collected at the bottom of the two columns, at the bottom of the first the less volatile component, and at the bottom of the second the highest volatile component.
The azeotropic distillation can be divided in two types based on the type of mixture to be separated: homogeneous or heterogenous azeotropic distillation.
The experimental set up change between them (figure 16).

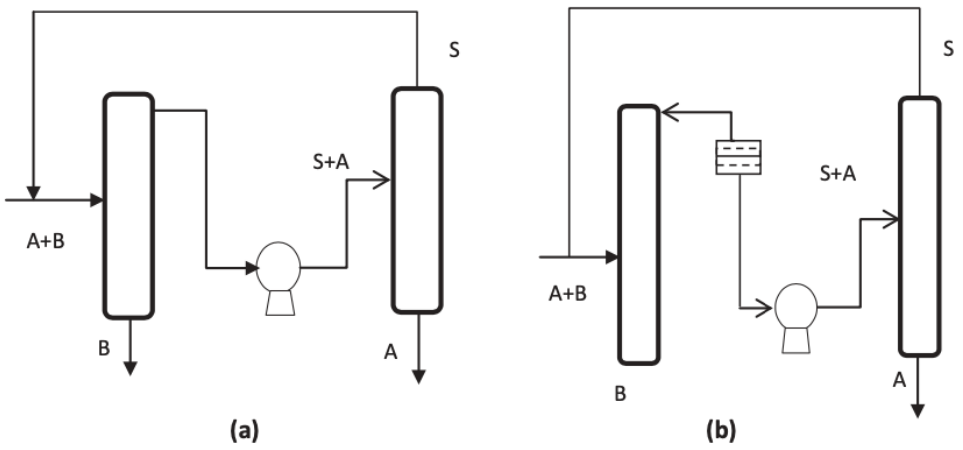

Figure 16 schematic representation of an azeotropic distillation, where A and B are light and heavy components of the feed mixture, S is an entrainer; a)homogeneous process, b)heterogeneous process. (T. Mahdi, 2014)

In the case of homogeneous process, phase split does not appear in the liquid along the column, unlike the heterogeneous process, where the two liquid phases exist in some regions of a composition space. In heterogeneous process a decanter is used to collect the condensed vapor and permit the separation of the two liquid phases. Usually, this two phase are the entrainer and the lighter component, so after the separation the entrainer is recycled. The other phase is fed to the second column to eliminate the dissolved entrainer. If there isn't a decanter, also the heteroazeotropic mixture is used as a homoazeotropic one. and at the same time. The liquid composition on a tray or a section of the column is replaced by the overall liquid composition. In a three-phase system the relative volatility is calculated by:

$$\alpha_{ij} = \frac{\gamma_i \Upsilon_i \theta_i p_i^0 (x_i^{II} - X_i)\Upsilon_j + (X_i - x_i^I)\gamma_j}{\gamma_j \Upsilon_j \theta_j p_j^0 (x_j^{II} - X_j)\Upsilon_i + (X_j - x_j^I)\gamma_i}$$

Where x_i^I and x_j^I are the solubility of component i and j in the upper liquid phase; x_i^{II} and x_j^{II} are the solubility of component i and j in the lower liquid phase. γ and Υ are the activity coefficient in the upper and lower liquid phase respectively. p_i^0 and p_j^0 are the partial pressure. θ_i and θ_j are correction factors for high pressure, but at low or moderate pressure the value can be approximated to 1. More the relative volatility differs from 1 more the separation will be easy (T. Mahdi, 2014).

Extractive distillation:

Involves a relatively nonvolatile entrainer. The entrainer is added continuously to the top of the fractionation column, in this way an appreciably high amount of entrainer is maintained on all plates in the distillation column. The entrainer (S) is removed from the bottom of the column with the component of the feed mixture (B) that interact with it. The component that does not interact (A) is collected from the top of the fist column. The bottom products are sent to a second column where the entrainer is collected from the bottom of the column and recycled in the first, while the second component of the feed mixture is collected from the top of the second column (figure 17a). Because of the large distance between the boiling temperature of the entrainer and the B component, usually the separation in the second column is easier. In some cases, dependently by the entrainer, the set up can have only one distillation column, and the entrainer is recovery with some other apparatus and not with a distillation column (figure 17b).

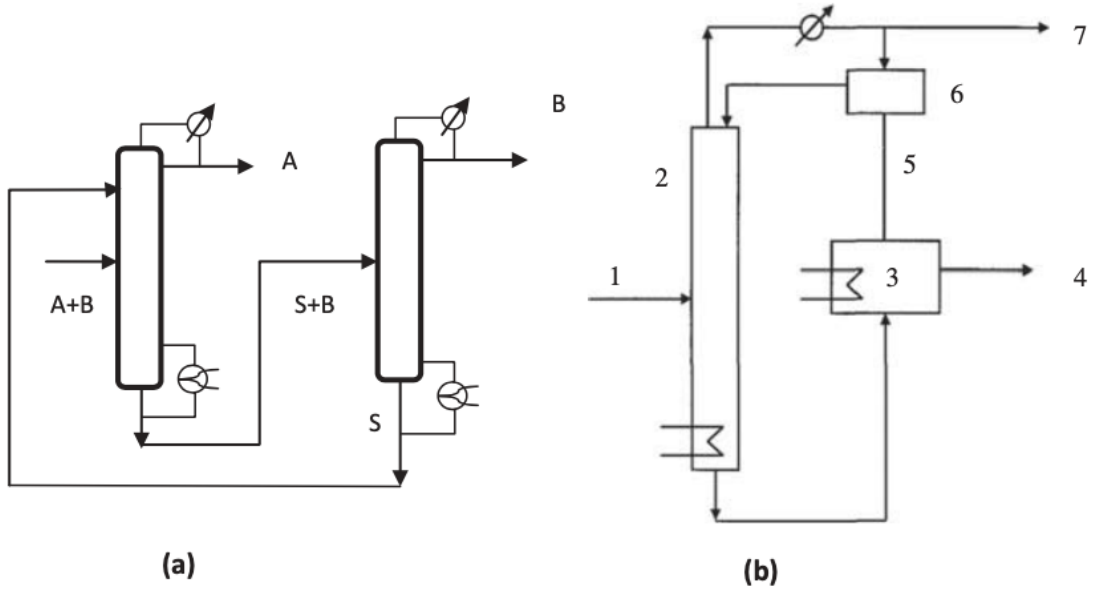

Figure 17 schematic representation of an extractive distillation: a) with two distillation columns, b) with only one distillation column; where 1is the feed stream, 2 is the column for the extractive distillation, 3 is the equipment for recovery the entrainer, 4 is the bottom product, 5 is the entrainer recovered, 6 is the reflux tank, and 7 is the overhead product. (T. Mahdi, 2014)

This type of distillation is more commonly used in industries due to lower energy requirement and wider selection of entrainers, but the products obtained are less pure than an azeotropic distillation. In fact, the product could contained some impurities (T. Mahdi, 2014).

It is possible to use different kinds of entrainers in an extractive distillation process. The entrainer influenced the mechanism and results of the separation; the main categories are:

- *Liquid solvent:* a high solvent ratio is used to obtain high performance from the system, thus leading to high energy consumption. The solvent can be recovery effectively under normal operating condition, so this is the preferred choice in industry (figure 18a)
- *Solid salt:* the separating agent is a solid salt which is fed at the top of the column, dissolved into the liquid phase, and recovered by evaporation (figure 18b). The salt must have some characteristics: it must be soluble in the feed components, nonvolatile and able to flow all the way down the column. The presence of this salt has the ability to alter the vapor composition in the equilibrium column due to the salt effect, which functions by modifying the relative volatility of the mixture. The feed component in which the equilibrium vapor is enhanced is said to have been ”salted out” by the salt, the other feed component is “salted in”. The phenomenon is described with the following equation:

$$\log\frac{S_0}{S} = K_s C$$

The Setschenow equation, where S_0 is the solubility of the salt in pure solvent, S is the solubility of the salt in a salt solution of concentration C (mol/L) and K_s is the salting coefficient, which has a characteristic value for a given salt-nonelectrolyte pair. If $K_s > 0$ it corresponds to salting out ($S_0 >$ S) if $K_s < 0$ it corresponds to salting in ($S_0 <$ S).

The advantages of using solid salts are: a more effective separating agent compared to the liquid one, the amount of salt required is smaller than the liquid one, the consumption of energy is smaller, and the production capacity is higher. Solid salt is not volatile so also the product of the column has a higher purity. And solid salts are environmentally friendly.

The disadvantages are: the solid salts cause the corrosion of the equipment giving an increase of maintenance costs, furthermore the salt decay easily at high temperatures; thus limiting the application of salt in the industrial process.

- *Combination of liquid solvent and solid salt:* the configuration of the system is similar to the system with liquid solvent (figure 17a); this is advantageous due to the easier operation offered by the liquid solvent scheme, but the performances of the separation are better because the presence of the solid salt. This technique is not common because the corrosion of the equipment is caused by the salt and because many salt decay easily at high temperatures, so a narrow range of suitable solid salts is available for selection.
- *Ionic liquid:* ionic liquid is composed of salts which are liquid at room temperature, to obtain this substance the right choice of the anion and cation is fundamental. These compounds are very useful in extracting distillation because they have a negligible vapor pressure at room temperature; this means that the obtained component on the top of the column is very pure, and also the risk to lose a part of this entrainer in atmosphere or the exposure risk for the operators is very low. The extracting distillation with ion liquids set up is very similar to the solid salt set up. It is possible to use this technique with both polar and non-polar solvent systems.

  the advantages of this technique are the absence of product impurities at the top of the column, suitability for use over a wide temperature range; from room temperature to above 300°C, suitability of ionic liquids for treatment with a wide variety of materials including organic, inorganic and polymeric materials, easy to recovery and recycling, high stability under operating conditions.

  Some disadvantages that make this technique not widely used are that: this technique must be tested more deeply, and the cost of the ion liquids is very high, the separation of viscous solution with ion liquids is very difficult, and finally ion liquids are moisture sensitive.

- *Hyperbranched polymers:* it is a class of highly branched macromolecules with a treelike topology and a large number of functional groups and three-dimensional polymers. This class of compounds are so useful because the presence of large number of functional groups within the molecule. The functional group allow to tune of their thermal, rheological and solution properties; that's allow the opportunity to design entrainers for a wide variety of application. The hyperbranched polymers show a remarkable selectivity and capacity, and also a low solution and melt viscosity and good

thermal stability. The application of this class of compounds is not tested deeply for an industrial use.

Pressure swing distillation:

Pressure swing distillation (PSD) is based on the fact that a change in pressure can alter the relative volatility of a liquid mixture; even for a liquid mixture that forms an azeotrope. If the operating pressure is increased, the azeotropic point shifts to lower composition values of the light component (figure 18). The positive change in the azeotropic point and enlargement of relative volatility of azeotropic mixture make it possible to do the separation without a separating agent.

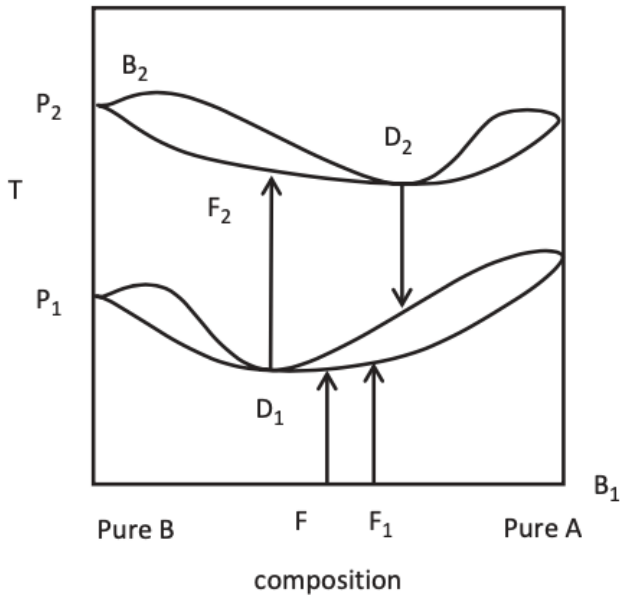

Figure 18 the impact of the pressure on a minimum-boiling azeotrope (T. Mahdi, 2014).

If the feed has a lower light component concentration than the azeotropic point, the feed is introduced into the lower pressure column, otherwise the feed is introduced into the high-pressure column.

PSD can work in three different modes: continuous, batch, and semicontinuous; the theorical principle is the same for the three methods (figure 18), change only the setup.

Continuous mode:

Figure 19 illustrates the separation of a binary mixture with a homogeneous minimum-boiling azeotrope in a continuous PSD. Because feed stream *F1,* which is a combination of the fresh feed F with the recovery stream *D2,* has a mole fraction of light component A greater than the azeotropic point, *F1* is fed into the low-pressure column (LP). The goal of this column is to concentrate component B near the azeotropic point of the mixture and to remove pure component A in the bottom of the column. The azeotropic mixture *D1* that leaves the top of the column serves as the feed stream *F2* to the second high-pressure (HP) column to produce pure heavy component B in the bottom of the HP column. The remaining products are recycled from the top to be mixed with fresh feed *F* to the first column. Both columns work with different pressures because to fit the goals that are required (T. Mahdi, 2014).

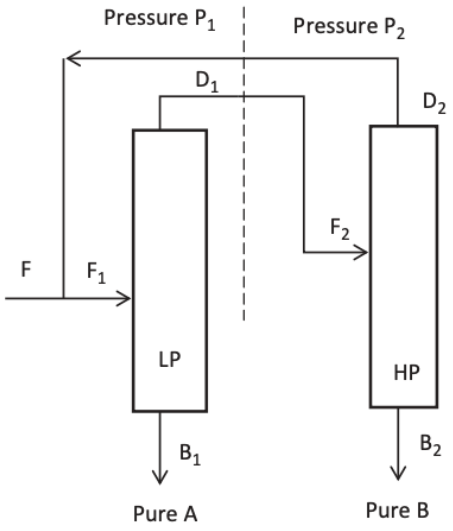

Figure 19 PSD in continuous setup (T. Mahdi, 2014)

Batch mode:

In a PSD that works in a batch mode is used only one column. The pressure is changed into the column. The process consists of two main steps. Between the two steps the pressure is changed. In the first step the feed (F) is stored in a thank at the bottom of the column; the pressure is the

lower or the higher one based on the composition of the mixture. The feed is introduced in the column; at the top of the column is collected the azeotrope. At the bottom of the column is collected one of the two components of the mixture. Step one is repeated until the wanted concentration of pure component is obtained. The pure component is collected in the feed tank. After step one the pressure inside the column is changed; the column is fed with the azeotropic mixture. The different pressure allows to obtain at the bottom of the column the second pure component, and at the top of the column the azeotropic mixture. Also, the step two is repeated many times until the wanted concentration of pure component is reached.

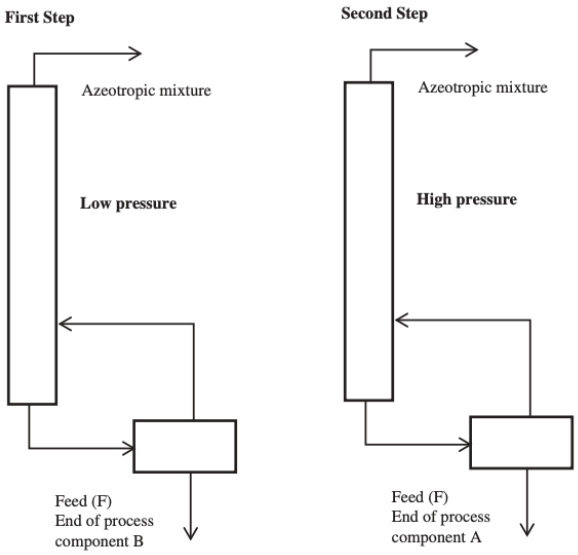

Figure 20 PSD in batch mode setup (T. Mahdi, 2014)

Semicontinuous mode:

The setup is composed of only one column, with some auxiliary tank. The first two tanks (tank 1 and tank 2, in the figure 21, near the top of the column) need to collect the feed mixture for the column. In one of them can be contained the original feed mixture, and in the second one can be contained the azeotropic mixture collected at the top of the column and subsequently used to feed the column and obtained the other component. The other two tanks (tank 3 and tank 4) are used to collect the pure component of the original mixture. A system of this type of work in two different modes, changing the feed source and the pressure inside the column. It

is called semicontinuous because the column works continuously, but with different feed sources and with different products both at the top and at the bottom of the column. When one feed source is used the other feed source is filled, and vice versa. In this way the system can work continuously. A stream is sent continuously to the reboiler, and cooling water is sent continuously to the condenser. The advantages of the semicontinuous mode respecting a continuous mode are: greater flexibility and lower investment cost.

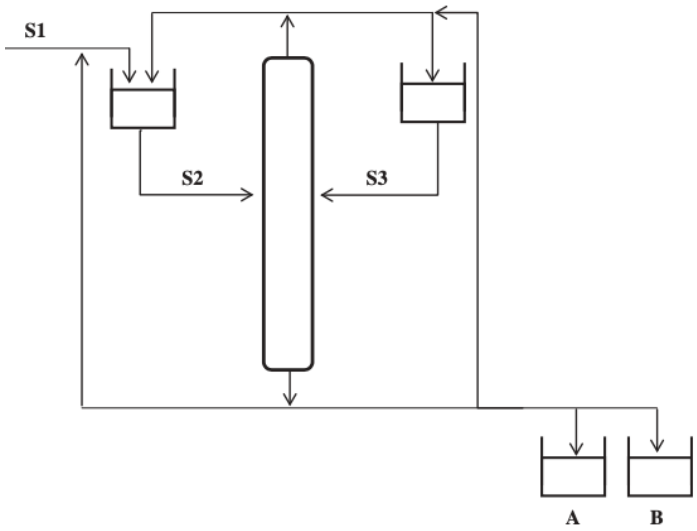

Figure 21 PSD in semicontinuous mode setup (T. Mahdi, 2014)

PSD process has some disadvantages: the setup and the work condition are more complex and difficult to obtain than the other possibilities, and the pressure, different from the atmospheric one, is harder to obtain and introduce it in a industrial context. For this reason, the data about its use in the industrial is few.

Membrane Technologies

Membrane based technologies have some advantages with respect to the other process used to resolve an azeotrope. They are considered clean technologies due to the lower energy demand and because it is not needed additional chemicals to obtain the separation. There are different types of membrane process, the most common is pervaporation.

Pervaporation:

Pervaporation involves permeation of the feed components through a membrane, followed by evaporation into the downstream at various rates. The membrane allows only one of the components of the feed mixture to permeate, in the other side of the membrane the permeated component is vaporized and collected somewhere else and then condensed (figure 22). The driving force of this process is the difference in the partial pressures of the components on the two sides of the membrane. This driving force is not affected by the relative volatility of the mixtures, and this is the main advantages of this process. The part of the mixtures that do not pass through the membrane is called retentate. There are also some disadvantages; this process is very slow because of the slowness of the mass transportation through the membrane. Also, the fact that the membrane is in direct contact with the feed mixture, and the other product is a problem; this fact could cause the swelling or shrinking of the membrane materials, and a decreasing of the performance of the system. Vaporizing the feed mixtures and permeating it through the membrane, the swelling or shrinking of the membrane can be prevented. A polymer with a great affinity with one component in the feed is preferred for making PV membranes to obtained higher selectivity; however, the membrane will become swollen if this affinity exceed a certain level, with a consequent membrane's integrity lose.

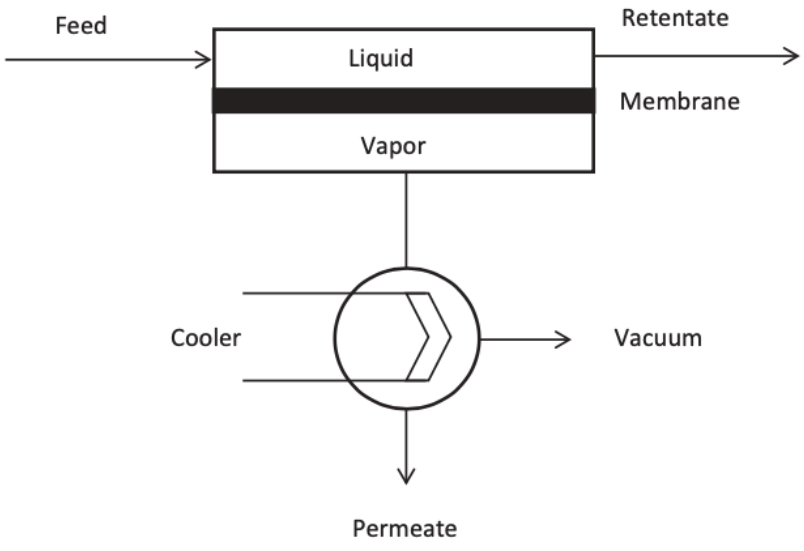

Figure 22 schematic refiguration of pervaporation process (T. Mahdi, 2014)

Frictional diffusion:

Frictional diffusion (FricDiff) is a separation technology based on differences of diffusivities in gas or vapor mixtures. The FricDiff consist in a feed gas separated by a non-selective porous membrane from a mass separating agent. This technology is able to break an azeotrope. This process decreases the use of energy and does not need the presence of other dangerous chemicals. As shown in figure 23 the non-selective membrane is positioned between a flux of feed mixtures and a flux of counter gas (separating agent). The components of the feed mixtures have different dimensions. The smaller component is easier to pass through the membrane and do it quicker than the bigger component. The counter gas needs to increase the difference velocity between the diffusion of the different components. The smaller component will be less hindered. In figure 23 the small component is the component A and the big component is the component B; the counter gas is called C. The flux of the counter gas and the feed mixtures are opposed in figure 23, but the system can work also when the two flux go in the same direction. This process is based on the difference in transport velocities of the components of the feed mixtures in the counter gas.

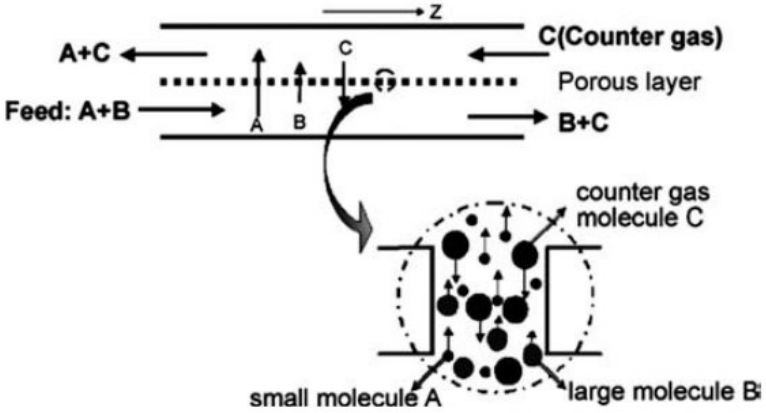

Figure 23 representation of the frictional diffusion separation technique (T. Mahdi, 2014)

Hybrid process Distillation/Pervaporation:

Using distillation and membrane together is possible to obtain better performance than using distillation or membrane process alone. This strategy is little used at the moment, and there is not many studies about its optimization in an industrial context. This process is called membrane distillation (MD).

In MD process a liquid solution at high temperature is brought into contact with one side of porous hydrophobic membrane that acts as barrier to separate the warm solution (feed side)

from the permeate in either a liquid or a gaseous phase, which enters in a cooling chamber called the permeate side. The hydrophobic membrane avoids the solution enters in the pores of the membrane and form an interface at the pore entrance. If there is a volatile component in the feed side it migrates through the pores in the permeate side of the membrane, because the temperature difference at the two ends of the pores produces a vapor pressure gradient within the pores. The migrated molecules that depend on the configuration of the membrane used are either condensed or removed in a vapor form from the membrane module. The solution from the feed side is concentrated.

MD is advantageous due to its low cost and low energy consumption but suffer from some drawbacks such as low permeate flux. There is different configuration for MD setup, in which change the position of the membrane respect the column, and also how the column and the membrane work together (figure 24)

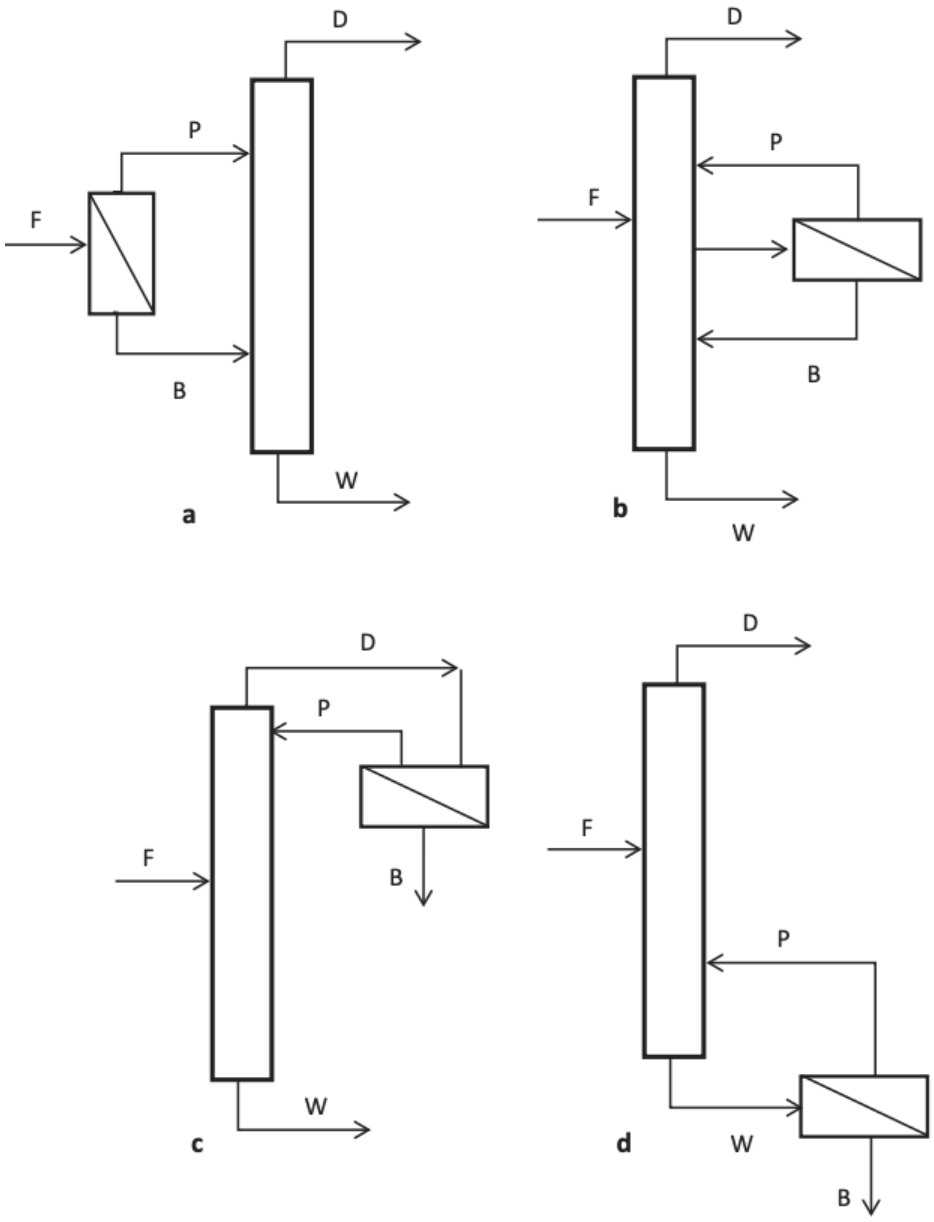

Figure 24 representation of various configuration of MD (T. Mahdi, 2014)

Process intensification

Process intensification technique are a group of techniques that leads to an increment of the performance of the separation process. These techniques are very studied because the energy saving, the smaller apparatus, the cleaner and safer condition. They are also used to increment the functionality of the process (dividing wall distillation), or to introduce a selected process phenomena into the conventional separation.

Dividing wall distillation column:

This technique is useful when there are more than two components in the feed mixture. To separate all the components in a mixture with more than two, normally are needed a number of columns equal to the number of components to separate. With the dividing wall distillation column (DWC) the number of columns can be decreased, saving space, energy and money.

The middle section of a DWC is split in two sections by inserting a vertical wall in a appropriate position. The latest improvement of this technology allows us to use a multiple column within the shell using non-welded wall technology.

Considering a mixture with components A, B and C; with A the lightest component and C the heaviest component; in a DWC column the component A and C will be separated normally, with the component A at the top of the column and the component C at the bottom of the column. Component B will be both in the top and in the bottom of the column with the other component. A liquid from the top section refluxes from the top in both the prefractionation and the main fractionator; the same thing will do by the vapor generated by the bottom of the column. In this way component B will be collected in the middle of the column in a selected stage of the main fractionator where the concentration of B is maximum (figure 25).

This technique is used in industrial sector, but it is not so common in the azeotropic resolution, where there are some theorical study about its performance, but not many experimental data.

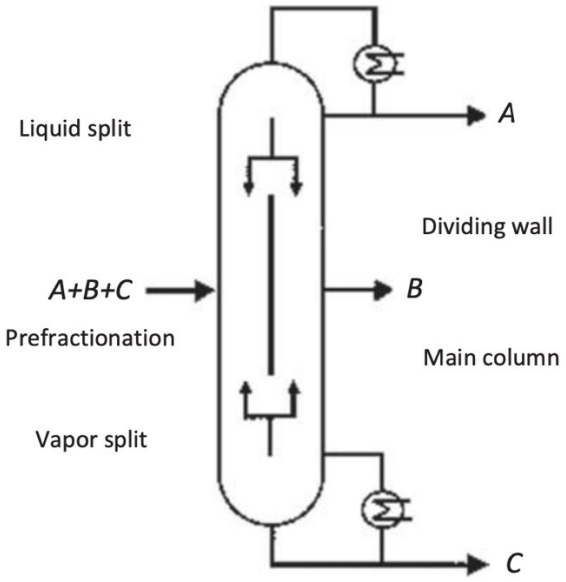

Figure 25 representation of dividing column wall distillation (T. Mahdi, 2014)

Microwave enhanced process

Microwave process is a way to heating, at a molecular level, solution and compounds that can absorb the microwave. The use of microwaves is common to increase the performance of some process: separation, desorption and drying. It is also used to intensify some reaction.
Microwaves can increase also the performance of distillation process in some conditions. The performances are improved when the microwaves interact directly with the vapor-liquid interface, or when only one component of the mixture absorb them while the other component do not interact with them, in that case the element that interact with the microwaves enrich the vapor phase and the other element enriched the liquid phase. A microwaves field can also modify the azeotropic point of an azeotropic mixture. If none of this condition is not respected the microwaves do not improve the performance of the distillation process.

Ultrasonic enhanced process

The ultrasonic are used in the chemical industry; in this field they are used for enhanced cleaning, separation and reaction process. The main causes that allows to ultrasonic waves to have an impact in these field are: heating, acoustic streaming and ultrasonic cavitation.
Ultrasonic waves can be useful also in enhancing distillation, and to resolve binary azeotropic mixture. These waves have an effect on the vapor liquid equilibrium (in binary mixture); they

can positively change the vapor liquid equilibrium and alter the relative volatility of the component's mixtures. This effect is caused by the cavitation activity during the transmission of ultrasonic waves in a liquid medium. The ultrasonic waves introduce energy in the liquid medium of the mixtures, producing microbubbles and a vacuum effect; in this way the heaty and mass transfer are very fast (because sonication is a fast transient). The ultrasonic waves do not produce significant net changes in the operating condition.

There are some advantages in using the ultrasonic waves: the azeotropic point can be eliminated with the right condition, it needed only one column during the separation process, it saves energy and it is no needed the use of other chemicals to obtain the separation, so it is safer and cleaner.

This process is not jet tested in an industrial environment.

What do we use?

In our case we have decided to waste a little part of the R134a to form the minimum azeotrope with the isobutane and to eliminate it in the vapor phase in a standard distillation. Because of the initial composition of the mixture, we waste only a little part of R134a. That allows us to obtain a maximum efficiency of 85.7%.

We use this technique because the setup system is relatively cheap and simple to build, and because it can manage a big volume of the gaseous mixture.

We'll go deeper in the setup system's explanation in the next chapter.

R134a recuperation system

The filling mixture of the RPC is composed by 95.4% of R134a, 4.5% of iC_4H_{10} and 0.3% of SF_6. These gases are very expensive and represent an environmental risk; in fact, they are powerful greenhouse gases.

It is really important to recuperate R134a for some reason. First of all, this gas is really expensive. Every year CERN spends around 230000 CHF for each experiment that use it to buy the needed quantity. The cost is so high not only for the big quantity that the CERN use, but also for the limitation that the UE establish to control and discourage the use of fluorinated gas. The fluorinated gas as R134a and also SF_6 , another component of the mixtures gas of the RPC system, have a global warming potential (GWP) respectively of 1430 and 23900, and this classified them as greenhouse gasses (GHG), that is why they represent also an environmental risk.

The EU "F^- gas regulation" has been recently established to control emission from this type of gas. Its aims are:

- Limiting the total amount of the most critical fluorinated gases that can be sold in the EU.
- Banning the use of fluorinated gases in many types of equipment where less harmful alternatives are available.
- Preventing emission of fluorinated gases from existing equipment by requiring checks, proper servicing and recovery of the gases at the end of the equipment's life.

To reduce the use, the waste and the cost of this type of gas the RPCs system in ALICE, ATLAS and CMS works in recirculating mode, where the gases after their using are purified and recycled back again in the RPCs. In this way also the emissions of these GHG are limited. Nevertheless, a non-negligible quantity of fresh mixture has to be continuously injected. The RPC system is the main contributor to the CERN GHG emission.

CMS RPC gas system

The gas system in CMS allows to make the filling mixture in the right way and its recirculation. Not all the mixture is recycled, but only the 86%, the remaining part is done with new gas, that has a high cost. The main parts of the gas system are: primary gas supplies, mixer, chamber distribution system, purifier, pump and return gas analysis, and R134recovery plant. The focus is to recuperate R134a because it is 95.5% of the entire filling mixture.

Mixer:

The mixer module is composed by three lines with the goals to regulate the sources of the three gases of the filling mixtures; each line has a mass flow controller that regulate constantly the exactly amount of gas needed to obtain the filling gas with the right composition. The maximum flow that the mass flow controller can reach is 1000 l/h. Because the leak in the detector level a big part of the gas is lost. To use and test the R134a recuperation system is needed to increase the input flow of the mixer to provide the gas without changing the performance of the detector.

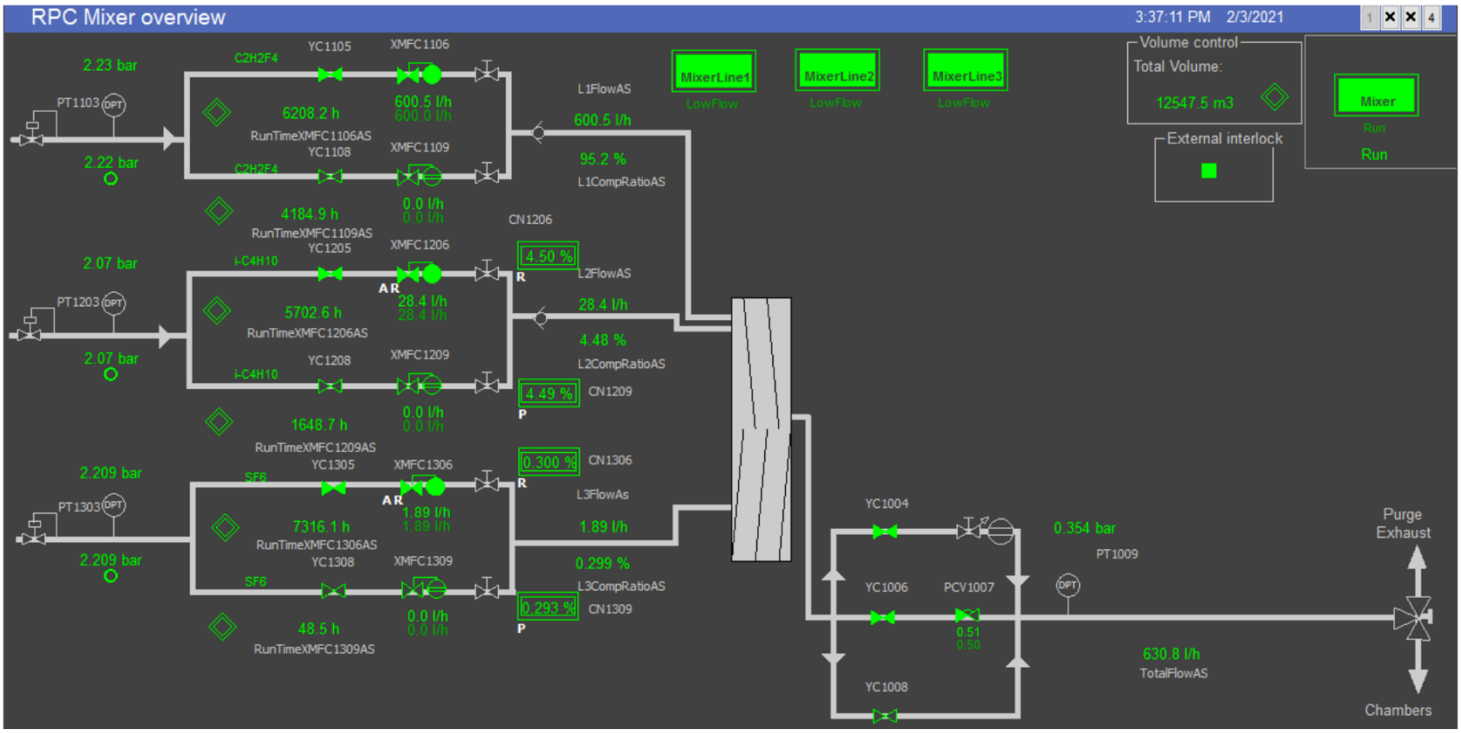

Figure 26 mixer's module control panel

Gas recirculation system:

It contains all the facilities that allow the recirculation of the gas, and allows to use only 10% of fresh gas. The recirculation system is distributed in three different areas:

- *The mixer room:* in the SGX1 building housing the input from the mixer, the purifiers and the recovery plant.
- *The US service area:* area where there are the chamber pressure regulation and the flow regulation for individual detector's wheel.
- *The experimental cavern:* (UX) containing the individual chamber gas distribution, channel flowmeter and gas sampling connection at the chamber outlets.

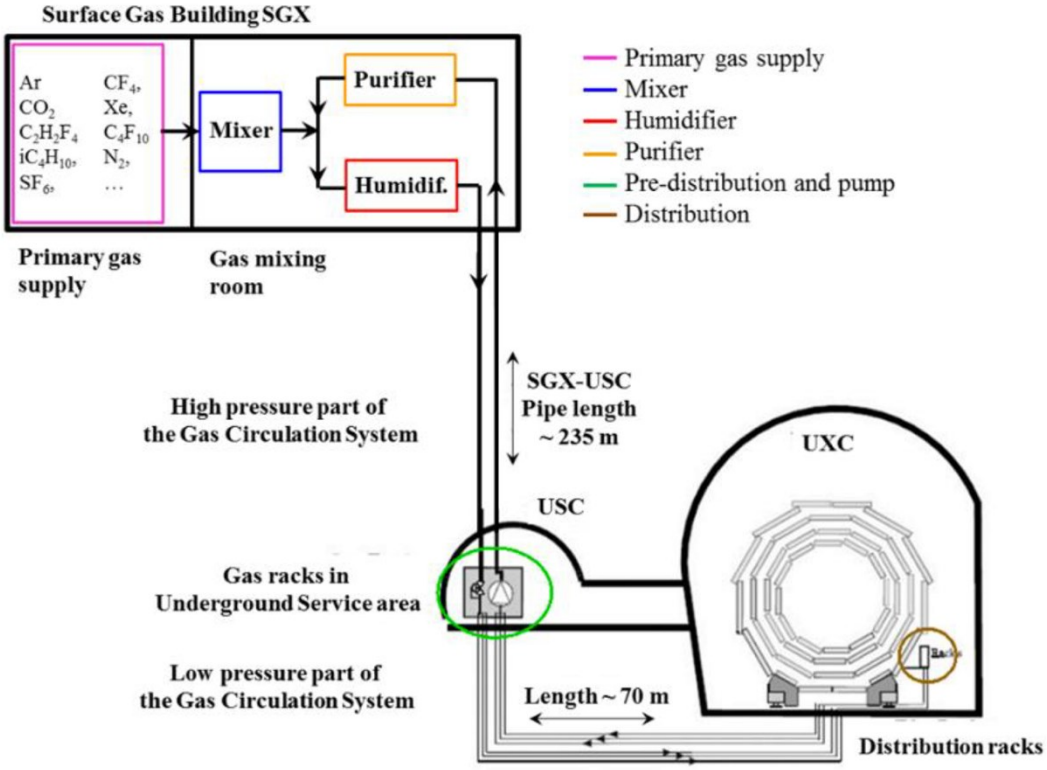

Figure 27 representation of gas recirculating system

Gas purification:

To allow the correct recirculation of the gas is required a purifier. The purifier has the goals to eliminate the impurities generated in the detector during the work. These impurities are: oxygen, water, halogens, hydrocarbons and nitrogen. The elimination of this impurities allows

to recycle the used gas. There are two purifiers (two columns each); one molecular sieve (MS) 10% 5Å/90% 4Å (Purifier 1, figure 28) and one 50% CuR11 and 50% $NiAl_2O_3$ (Purifier 2).

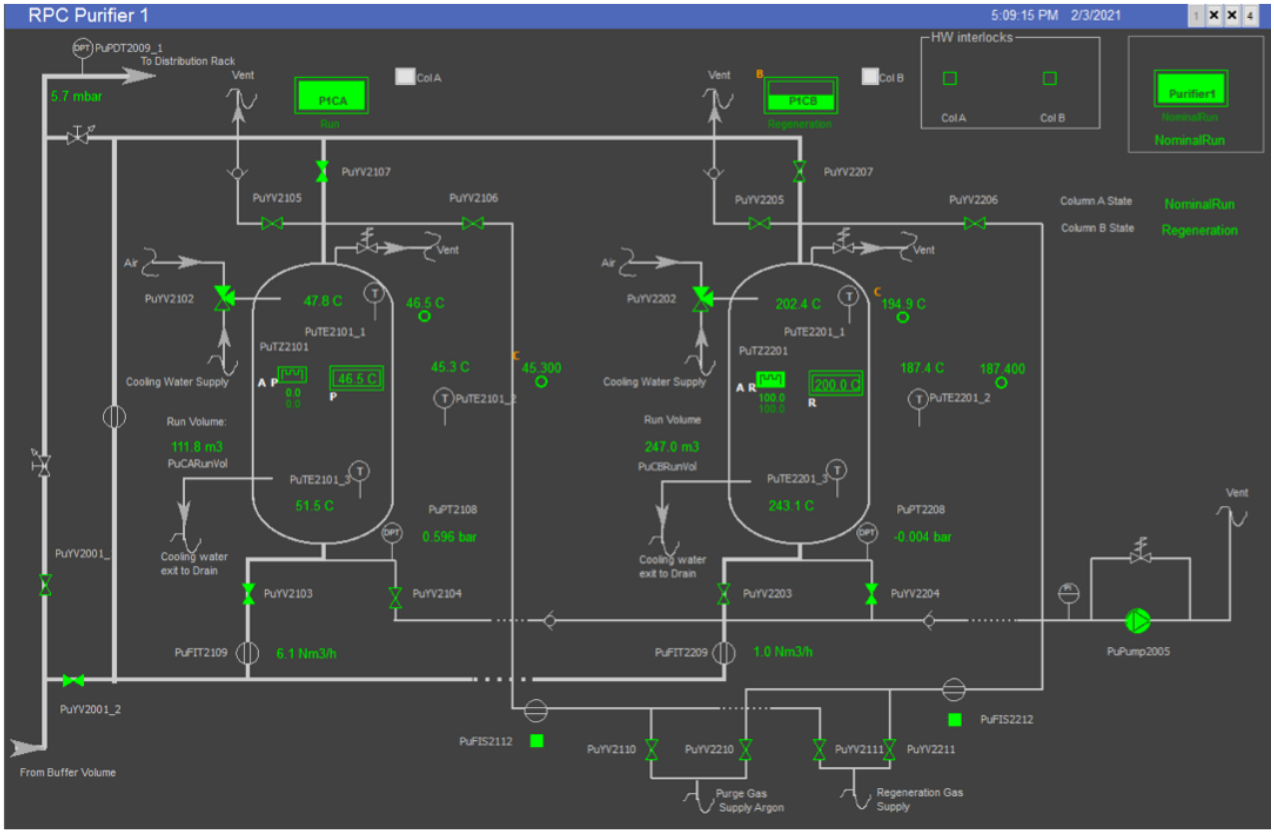

Figure 28 first purifier's control panel

The first purifier eliminates the water and some other specific impurities, for example fragments of R134a and HF. The second purifier eliminates oxygen and all the other impurities inside the recycled mixture. The elimination of the water is important because the mixture must have always the same concentration of water; this concentration of water is granted by the humidifier. After the two purifier the gas goes to the exhaust; the gas coming from there is used in the R134a recuperation system.

Principle of operation and recuperation system structure

the separation process has three main step; in the first step the gas mixture pass through the first heat exchanger where it is cooled at a temperature far below the 0 to condensate the R134a

and the isobutane, and to eliminate the SF_6 , air and nitrogen that have a lower condensation temperature, the second step has the goal to separate the R134a from isobutane; and the third step consist to collect the pure R134a in a storage bottle. The first and the third step work very well, and no problem is found. The second step is the tricky one, in fact the isobutane and the R134a form a minimum boiling azeotrope, of composition 65/35; because the R134a molecules interact with the isobutane molecule. The pressure inside the buffer 2 and 3 is constant and it is atmospheric pressure, so it is possible to form a temperature composition chart that represent the minimum boiling azeotrope of the mixture (figure 29)

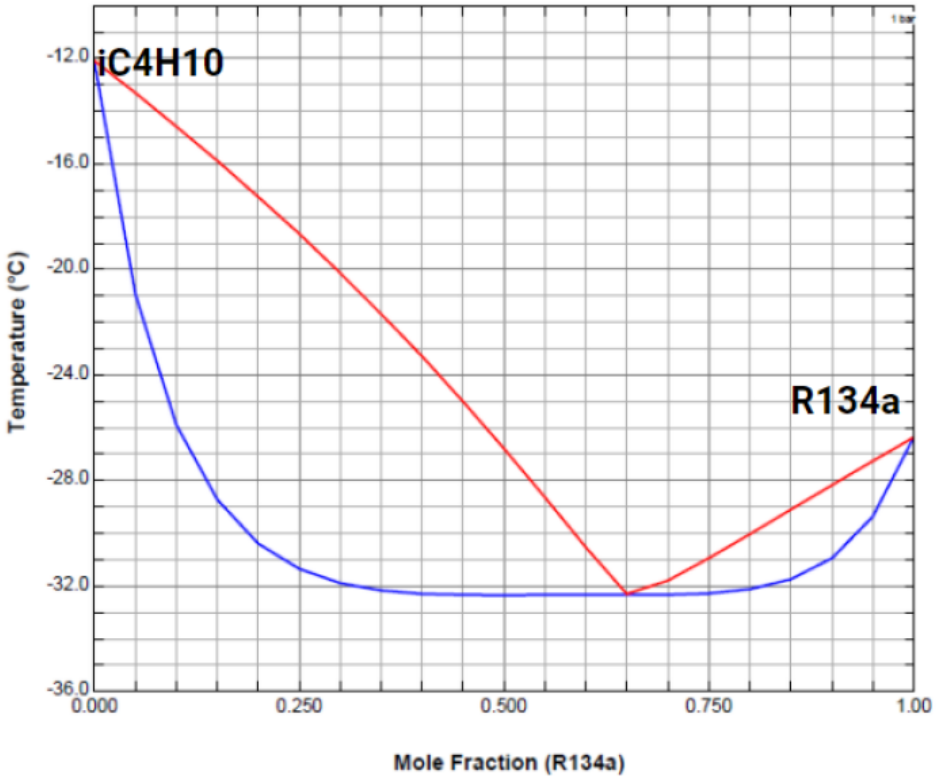

Figure 29 R134a/isobutane temperature composition chart (Cambie, 2021)

The starting composition of the mixture is 95/5 r134/isobutane at -32,5°C, which means that the starting point is in the right lobe of the chart (figure 29). Distilling this mixture, the liquid phase will be enriched in R134a and the vapor composition tends to be the azeotropic composition. Eliminating the vapor phase is possible to eliminate the isobutane with the compromise to waste a little part of R134a to form the azeotrope and to eliminate it. If the starting composition were placed in the left lobe, to obtain the pure R134a the procedure would be much more complex. In our case we can consider the mixture as a mixture with an ideal

behavior, but the two components are the azeotrope as the lightest one with a lower boiling temperature and the R134a the component with the higher boiling temperature.

Recuperation system structure

The recuperation system is divided into 2 parts. Each part is composed of 2 buffers and one thermal exchanger. The first part is composed of the thermal exchanger HX2; the two buffers are buffer volume 2 and buffer 3. The valve HV005 divided the two parts. The second part is composed by the thermal exchanger HX1 and the buffers 1 and 4; after buffer 4 there are one compressor and one storage bottle. The mixture inside the storage bottle can be analyzed with a GC (figure 30)

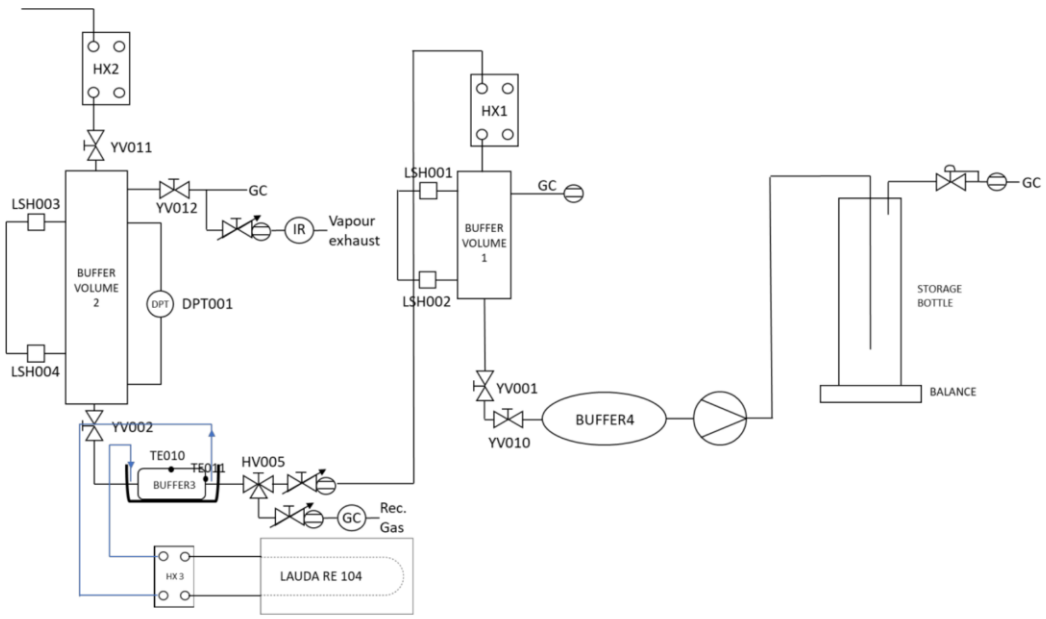

Figure 30 schematic representation of R134a recuperation system

Firstly, the buffer 2 is filled; the input flow is variable and the operator can set it; the maximum input flow available is 1000 l/h. The first thermal exchanger, set on a temperature of -35,5°C, liquefies the mixture, and in particular R134a and isobutane. SF_6, N_2, and air have a lower condensation temperature, so they are eliminated as gas from valve YV012; the valve YV002 is always open; the liquid mixture from buffer 2 is collected in buffer 3. Buffer 3 is inside a water/glycol bath. The temperature of this bath is controlled from 4°C to 6°C. The temperature of buffer 3 is very important, in this buffer takes place the separation; its temperature is controlled with the heat exchanger HX3, cooled with the LAUDA RE 104. The azeotrope, which has a boiling point lower than the R134a, enriched the vapor phase, the consequence is

that the liquid phase is enriched in R134a. The vapor phase is sent to the exhaust. When the buffers 2 and 3 are filled, the mixture is sent to the buffer 1, through the thermal exchanger HX1, it is also set on a temperature of -35,5°C, opening the valve HV005, where it is liquefied again. After the filling of buffer 1 the valves YV001 and YV010 are opened, the compressor is turned on and the storage bottle is filled.

The separation takes place only in the first part of the system where the vapor can be collected and eliminated from the top of the buffer (in buffer 2). In buffer 1 there is no way for the vapor phase to escape from the liquid and the buffer 4 is hold at ambient temperature and it is not regulated. The pressure inside the buffers 2 and 1 is measured constantly and there are also two sensors' level each buffer (buffer 1 and 2) to measure when the buffers are full or empty (buffer 1 is represented in figure 31 the sensor level are LSH001 and LSH002, but there is not the exit for a possible vapor in the real system).

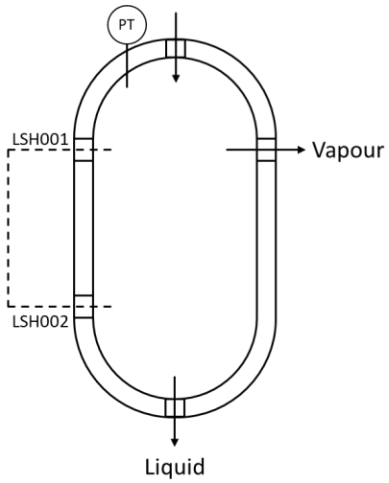

Figure 31 buffer 2 representation

Buffer 3 has two temperature sensors: TE011 below the buffer, and TE010 above the buffer.
Buffer 2 has also an additional pressure sensor that measures the differential pressure inside it and allow to monitor the filling of the buffer itself.
After buffer 1 there is the compressor that stores the obtained liquid in the storage bottle. The content of the storage bottle is sent to a GC and analyzed.

GC working principle

A gas chromatograph allows to separate the different mixture's components; the samples must be introduced as gas. It is based on the principle that different molecules have a different

affinity with the stationary phase inside the column. Usually, stationary phase is a liquid substance that coated a stationary support (a solid phase on the capillary's walls) inside the column, or directly on the column's walls, in this way the different molecules will be eluted in different time, and dependently by the detector used it is possible to detect them. There is a mobile phase to carry the sample through the columns. The carrier is a gas that do not interact with the component of the sample. It has the only goal to carry the sample through the column (figure 32).

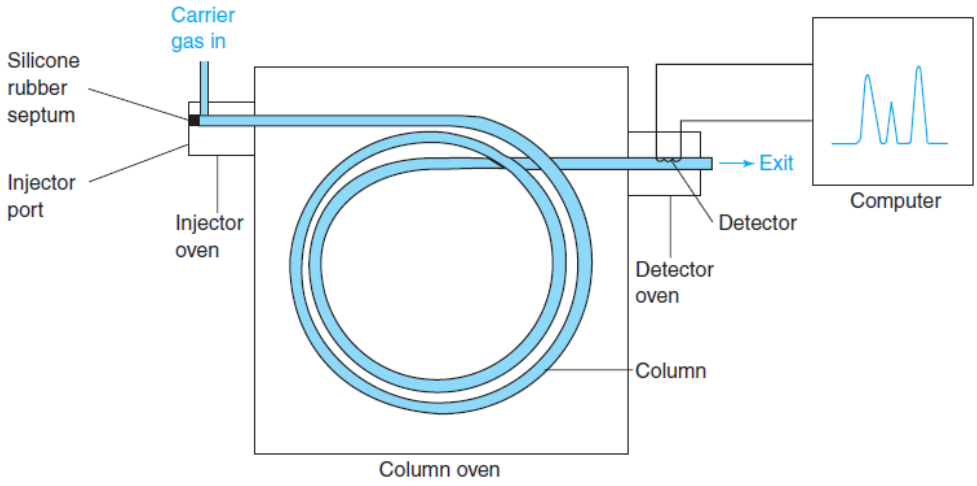

Figure 32 GC schematic representation

The most commons carrier gases are: helium, argon, nitrogen. All these gases are inert. The column and the injection system are heated to be sure that the sample inside the GC is in vapor condition. Moreover, the injection system must guarantee a rapid vaporization of the samples. (Holler & Crouch , 2015)

The GC used in this experimental work is an Agilent 3000A microGC it has two columns:

The type of column A is poraPLOT U, Porous Layer Open Tubular column. The stationary phase is Divinylbenzene/Ethylen glycoldimethacrylate; it is designed to separate halogenated compounds and hydrocarbons C1-C6 ketons and solvents. The column's length is 8m, and the carrier gas is helium. In this column there is a solid support on the column's walls and the stationary phase absorbed on it.

Type of column B is molecular sieve 5Å is a molecular-sieve-coated PLOT capillary column especially suited for high-resolution separation of permanent gases. The column's length is 30m and the carrier gas is argon. (Anon., s.d.)

The molecular sieve is an organic or inorganic porous materials, the different molecules of the sample could enter entirely, partially or not enter et all in this porous dependently to their dimension. The more a molecule enters into the porous more its retention speed is slowed down.

The detector used is a thermal conductivity detector (TCD), it measures the thermal conductivity, the capacity of a substance to transport heat from a warm zone to a colder one. The hot element that allow to measure the thermal conductivity is a metal filament (the most common metal used are tungsten), the reference value is measured with only the carrier gas in the detector (in our case one detector with helium and the other one with argon) when the analyte emerge from the column the conductivity of the gas stream change, and the filaments warm up, higher the temperature higher the electrical resistance. Measuring the variation in the resistance of the filaments, the different elements are detected. (figure 33) (Skooge, et al., 2009)

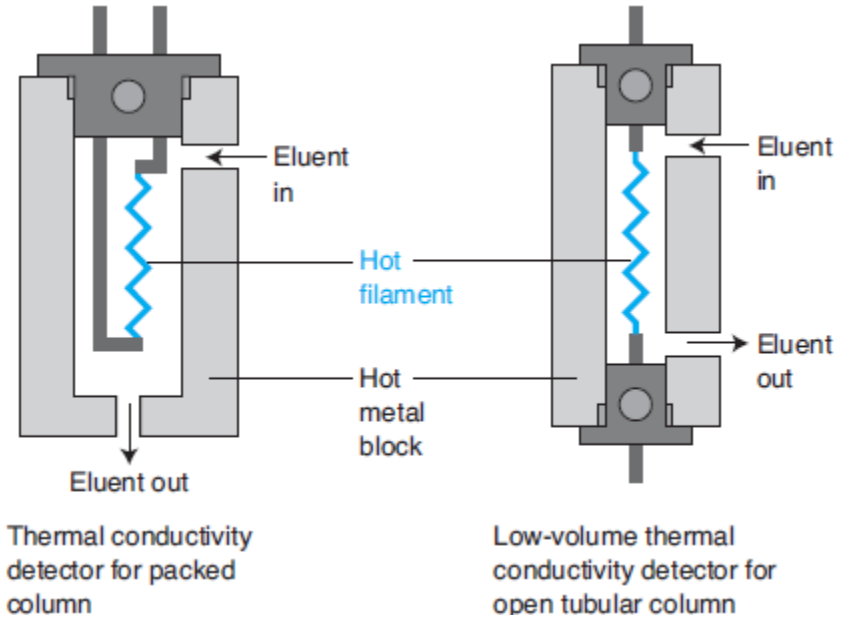

Figure 33 TCD configuration

Experimental setup

Starting point

In the previous work they studied the temperature of the thermal exchangers and the temperature of buffer three, the relative position of the two buffer and if the input flow changes the performance of the system.

The results of the previous work are:

- The input flow does not influence the performance of the system. It was tested from 100 l/h to 400l/h
- The best way to control the buffer three temperature is with a water/glycol thermal bath. The temperature of the bath is controlled to 4.5°C
- The best position for buffer 1 and buffer 2. They have different dimensions so, if the mixture enters first in one or in the other can influence the performance. The best results are obtained when buffer 2 is the first buffer (buffer 2 is bigger than the buffer 1) and it is connected to the buffer 3. After that there is the buffer 1 connected to the buffer 4.
- The best temperatures for the two thermal exchangers are: -35,4 °C for TE003 and -32,5°C for TE007

With this condition the concentration of isobutane is maximum 0,01% and the concentration of air is 20ppm (figure 34) (Cambie, 2021).

These conditions are used at the beginning of this work to reproduce the results of the previous work.

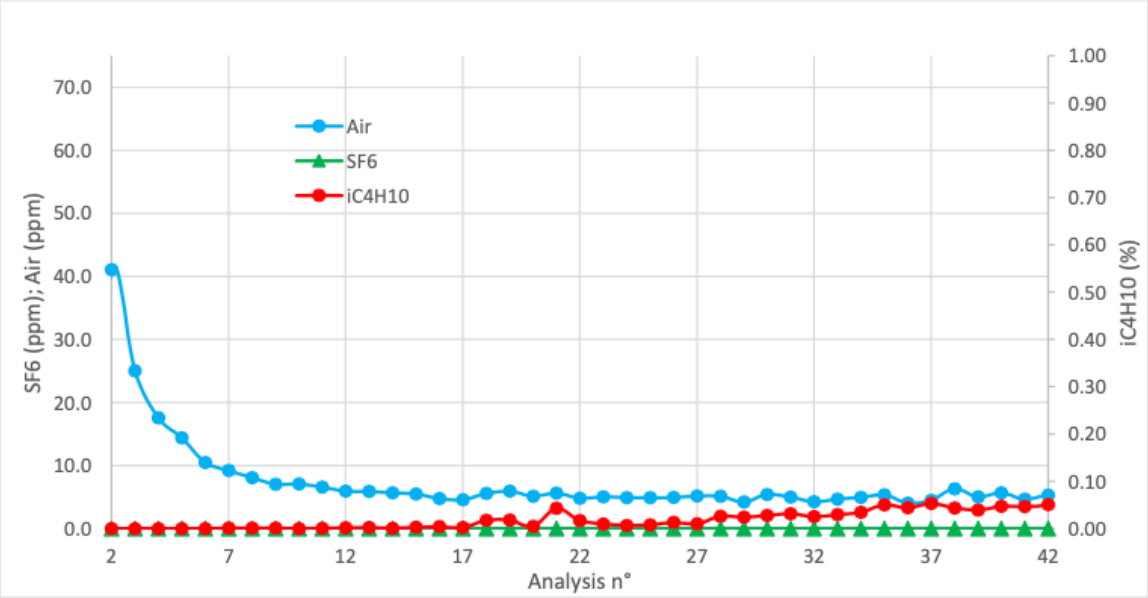

Figure 34 test 12, 6th cycle GC analysis (Cambie, 2021)

Experimental work presentation

This experimental work can be divided in different phase:

- Part 1: testing if higher input flow does not influence the results without the compressor using the batch mode of the system.
- Part 2: testing the continuous mode of the system without the compressor.
- Part 3: testing the continuous mode of the system with the compressor.
- Part 4: using the batch mode of the system with the compressor.

Table 1 total test's list

part 1	part 2	part 3	part 4	part 4
test I	A	1c cont	1c	10c
test II	B	2c cont	2c	12c
test III	C	3c cont	3c	13c
test IV	D	4c cont	4c	14c
1A		5c cont	5c	15c
2A		6c cont	6c	16c
3A		7c cont	7c	17c
3B		8c cont	8c	18c
4A			9c	19c
4B				20c
5A				
5B				

Part 1: **(1.0)** because the system is turned off for some months the first tests are performed to verify that the previous results are reproducible. From test I to test IV they are performed with only the first part of the system, so after buffer 3 the mixture is sent directly to the GC's input without the compressor thanks to a new line that connect the output of the buffer 3 to the input of the GC (figure 35).

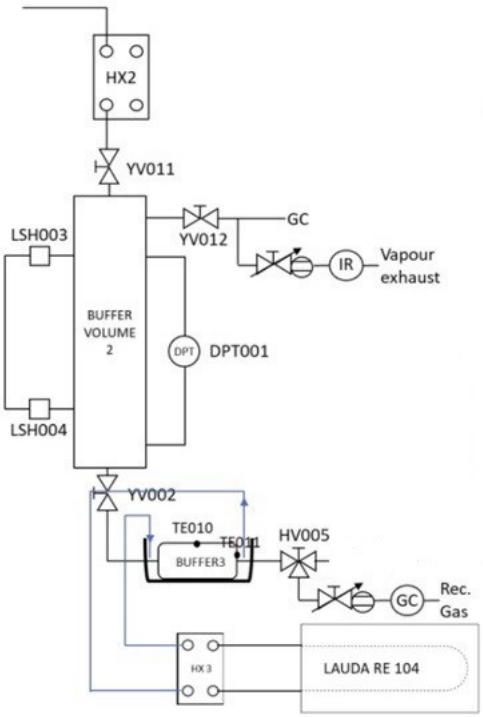

Figure 35 part 1.0 system setup

(1.1) from test 1A to test 5B they are performed with the entire recuperation system so, also with buffer 1 but without buffer 4 (figure 36). The mixture is sent to the GC's input after the buffer 1 without the help of the compressor because of some problems with it. Buffer 2 is bigger than buffer 1 so with only one filled buffer 2 we can fill buffer 1 two times. In table 1 the name of the test with A are the first filling of buffer 1, and the tests with B in the name are the second filling of the buffer 1. During this test the input flow is changed to verify again that the input flow of the mixture in the system doesn't change the performance of the recuperation. The maximum input flow tested is 600 l/h.

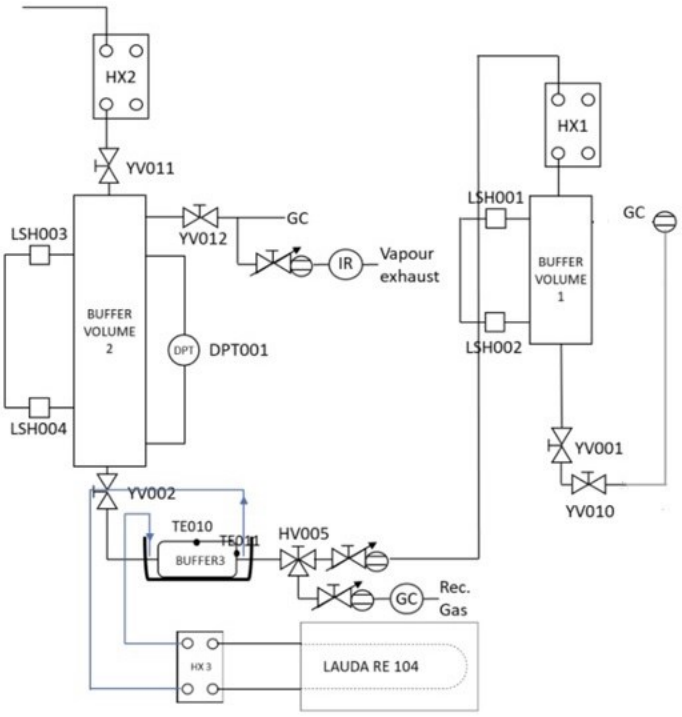

Figure 36 part 1.1 system setup

Part 2: from test A to test D the system is used in continuous; to do so we opened the valves HV005, YV001 and YV010, and after the valve YV010 we have a line that go to the GC, while the buffers 2 and 3 are filling (figure 36), the input flow that go inside the system is always regulated to avoid that the system was totally filled.

Part 3: **(3.0)** the system setup is shown in figure 37; after the valve YV010 there is a line that connects buffer 1 with buffer 4; it is connected to the compressor, which fill the storage bottle. From test 1c cont to test 3c cont they are performed with the filling status of buffer 2 variable. The test starts with a differential pressure inside buffer 2 of 25 mbar, and during all the test the differential pressure can change; It is not controlled.

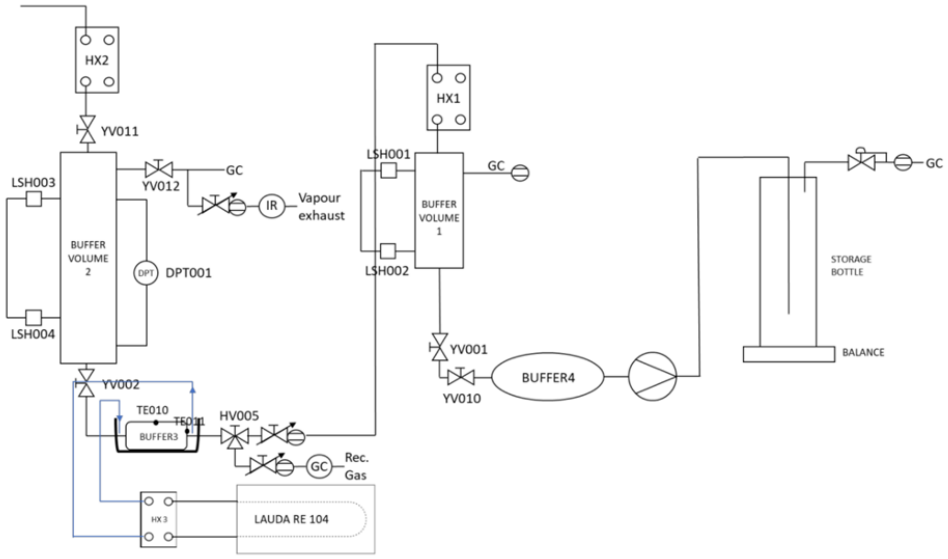

Figure 37 part 3 and 4 setup system

(3.1) from test 4c cont to test 6c cont they are in continuous with the compressor but maintaining the filling status of the buffer 2 constant and full (around 33 mbar as differential pressure inside the buffer).

(3.2) test 7c cont and 8c cont are performed not only with the filling status of buffer 2 constant and full, but also with the temperature of the bath of the buffer 3 controlled and regulated.

Part 4: **(4.0)** the system setup is shown in figure 37; all the buffers are used; after buffer 4 there is the compressor that fill the storage bottle. From test 1c to test 3c no experimental parameters are regulated, but the system works at full speed with the condition optimized in the previous work.

(4.1) From test 4c to test 8c we regulate the mixtures flow between buffer 2 and buffer 1.

(4.2) From test 9c to test 16c we regulate the mixtures flow between the 2 buffers and also the minimum liquid level inside the buffer 2, which is 20mbar.

(4.3) From test 16c to 20c we have controlled the temperature of the bath of buffer 3.

Results and discussion

Part 1: batch mode without compressor

1.0) In these tests we do not us the compressor; the transfer of the mixture until the GC is very slow.

Also with only one part of the system the performances are comparable to the last performance of the previous work (figure 36).

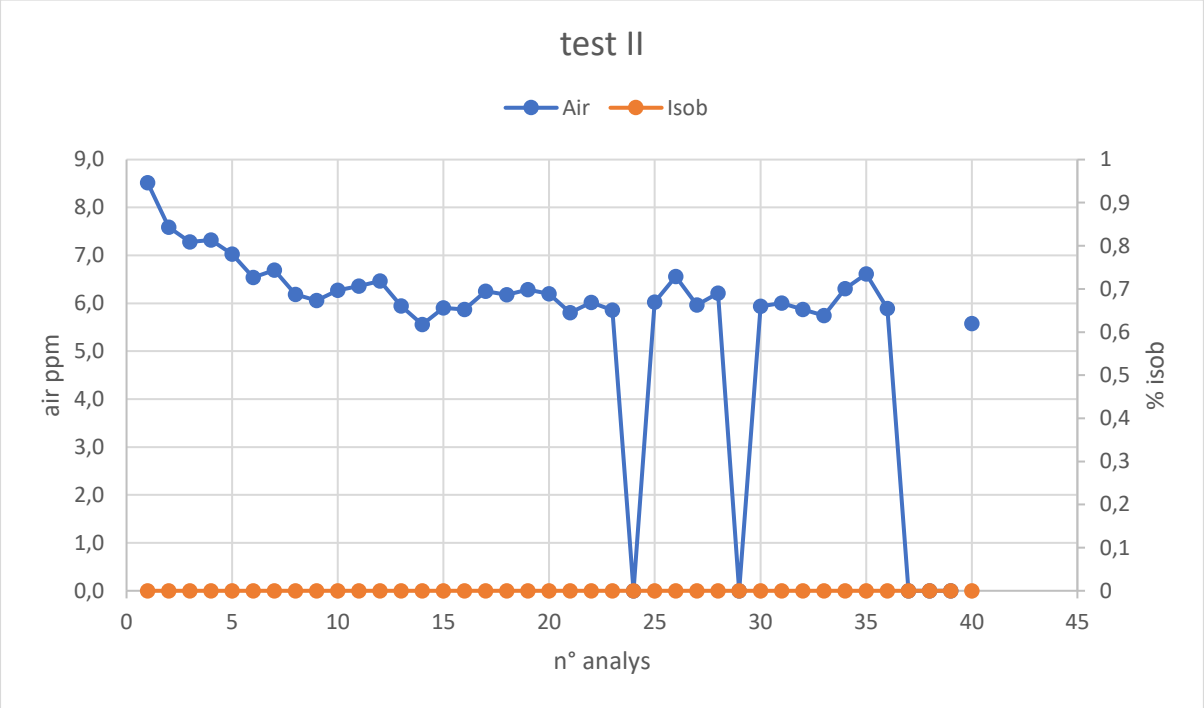

Figure 38 %isobutane and %air in the test II

Test II is performed with an input flow of 100 l/h; the concentrations of isobutane and SF_6 are 0%, the average concentration of air is 5ppm, revelated with the ppu column.

The other tests (test I, III and IV) have similar results even if the inputs flow are different; in particular there are not isobutane and SF_6 , the air is around 3.5ppm (table 4)

These performances are a little better than the performances of the previous work, this can be possible because the absence of the compressor has the consequence that the transfer time of the liquid mixture to the GC is higher so the liquid mixture wait more time in the buffer 3 where the separation takes place. Moreover the compressor add some air to the mixture so the concentration of air is smaller than the tests of the previous work.

1.1) After checking that the system works also with only the first part, we performed some tests with both the parts, changing the input flow to verify that also higher fluxed do not influence the performance of the system.

Table 2 part 1.1 tests to verify the input flow influence

Name	Mode	Input flow (l/h)
1A	batch	400
2A	batch	400
3A	batch	400
3B	batch	//
4A	batch	400
4B	batch	//
5A	batch	600
5B	batch	//

The maximum input flow tested is 600 l/h, the aim was to test also 800 l/h, but the mass flow controller of the mixer has some problem when the flow is so high. To avoid making some damage on the principal recirculating loop the 800 l/h is not tested.
All the tests performed with an input flow of 400 and 600 l/h have the same results (table 4).

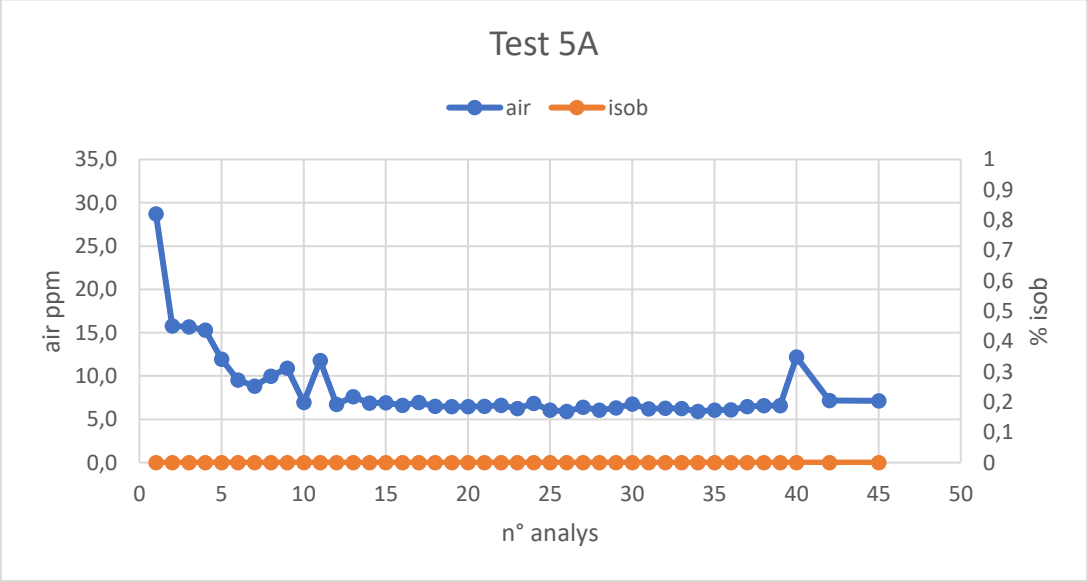

Figure 39 test 5A, input flow 600 l/h without compressor

Test 5A is an example of this kind of test, the input flow is 600 l/h the highest possible with the used instrumentation. There are no isobutane and SF_6, the average concentration of air is 10 ppm (figure 39).

The efficiencies of the test performed with the entire system (tests from 1A to 5B) are calculated and its average value is around 84% (table 3)

Table 3 test 1A-5B efficiency

Name	Input flow (l/h)	V injected (l)	V converted (m^3)	Efficiency (%)
test 1A	400	460	//	//
test 2A	400	440	//	//
test 3A	400	600	0,29	83
test 3B			0,20	
test 4A	400	607	0,30	83
test 4B			0,21	
test 5A	600	550	0,30	87
test 5B			0,18	

To calculate the efficiency, we have measured the total volume of the mixture injected into the system and confronted it with the gas volume sent to the GC input (measured with a flowmeter). The volume put inside buffer 2 is analyzed in two different tests (tests A and B with the same number ahead) so to calculate the efficiency of the procedure we calculate the total efficiency for both test A and B. For the first two tests we do not have analyzed the entire volume of buffer 2 so we can't calculate the efficiency.

Part 1 concentration of air and isobutane summary

Table 4 part 1 tests results list

Name	Isob(%)	Air (ppm)
I	0	20
II	0	5
III	0	10
IV	0	10
1A	0	10
2A	0	10
3A	0	10
3B	0	10
4A	0	10
4B	0	10

5A	0	10
5B	0	10

all the tests show that the separation is possible and there are not performances differences between the use of only one part or both part of the system.

Part 2: continuous mode without compressor

Part 1 has shown that the velocity of the process is very low without the use of the compressor (around 7 hours to fill the system and analyze all the output gas). We try to use the system in continuous because the time that the mixture waits in the buffer 3 before the analysis is very much and also the transfer between the buffer 2 and 1 is very slow. Also if the system works in continuous the time is sufficient for the separation to take place as shown in figure 40; the concentration of air and isobutane for each analysis are pretty constant.

The list of tests made in this way is reported in table 5

Table 5 test in continuous without compressor list

Name	Mode	Input flow (l/h)
A	continuous	100
B	continuous	100
C	continuous	200
D	continuous	150

The factor that limits tests in continuous is the transfer velocity between the buffer 2 and buffer 1; the flow between these two buffers is maximum 200 l/h so the input flow in the system can be maximum the same. This slowness permits the separation to take place also in a continuous mode.

The results of this test are comparable between them. The average concentration of air is 20 ppm; instead, isobutane and SF_6 are not present.

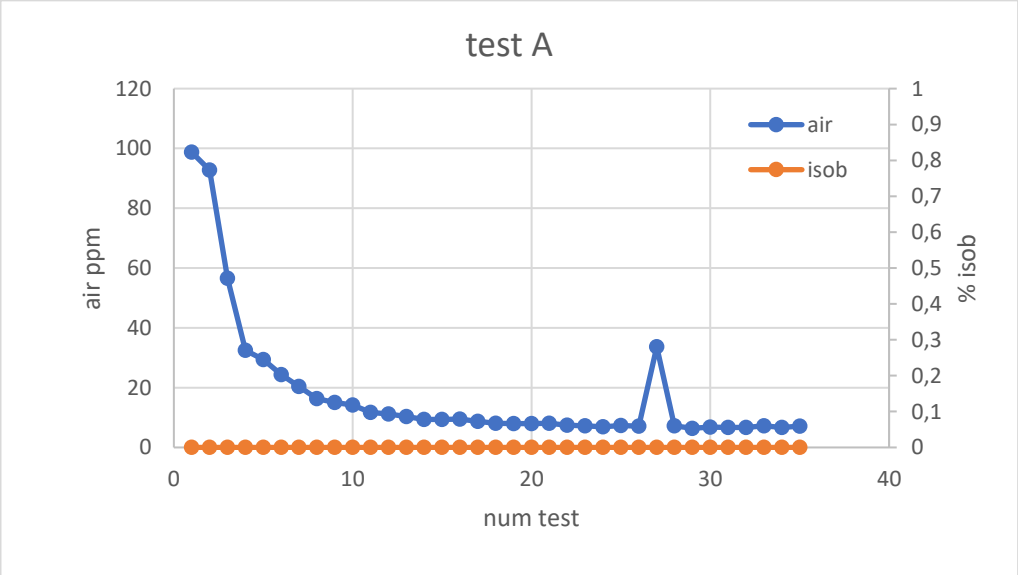

Figure 40 test A, input flow 100 l/h, continuous mode without compressor

Summary of the tests in continuous mode without compressor:

Table 6 resume tests list in continuous without compressor

Name	Input flow (l/h)	h of works	V tot treated (m^3)	Isob(%)	Air (ppm)	Efficiency(%)
testA	100	3	0,238	0,000	18	79,3
testB	100	4	0,318	0,000	18	79,5
testC	200	5,1	0,839	0,000	8	82,3
testD	150	4	0,469	0,000	24	78,2

As shown in table 6 not only the concentration of isobutane and air are comparable to the results obtained during part 1, but also the efficiency of the tests is very similar. The efficiency is calculated with confronting the total volume injected in the system with the total volume analyzed with the GC (V tot treated in table 6)

Without the compressor also the continuous mode is an available choice for the system. And we have demonstrated that the system can work in continuous with the right settings. However, the compressor needed to store the gas obtained from the recuperation system in the storage bottle. Without it the entire system is useless.

Part 3: continuous mode with compressor

Because of the success with the continuous mode without the compressor we have tried to use the system in continuous with the compressor.

Table 7 part 3.0 and 3.1 tests' list

Name	Mode	Buff 2 Filling status
1c cont	continuous	Variable
2c cont	continuous	Variable
3c cont	continuous	Variable
4c cont	continuous	Stable (full)
5c cont	continuous	Stable (full)
6c cont	continuous	Stable (full)

3.0) The results of this test are not good, in fact not only the concentration of air is very high, but also the SF_6 is present in the recuperated mixture; however, the concentration of isobutane is acceptable when the input flow in buffer 2 (and so the flow between the two buffers) is lower than 400 l/h. (table 8)

Table 8 part 3.0 results list

Name	Flow buff 2-1(l/h)	Isob(%)	Aria (%)	SF_6 (ppm)
1c cont	400	0,40	5,29	30
2c cont	200	0,05	3,48	20
3c cont	200	0,08	9,59	70

We can take as example test 2c cont; Isobutane and SF_6 concentration are stable through all the analysis, the concentration of the air decrease during the analysis but it is never lower than 2% (figure 41)

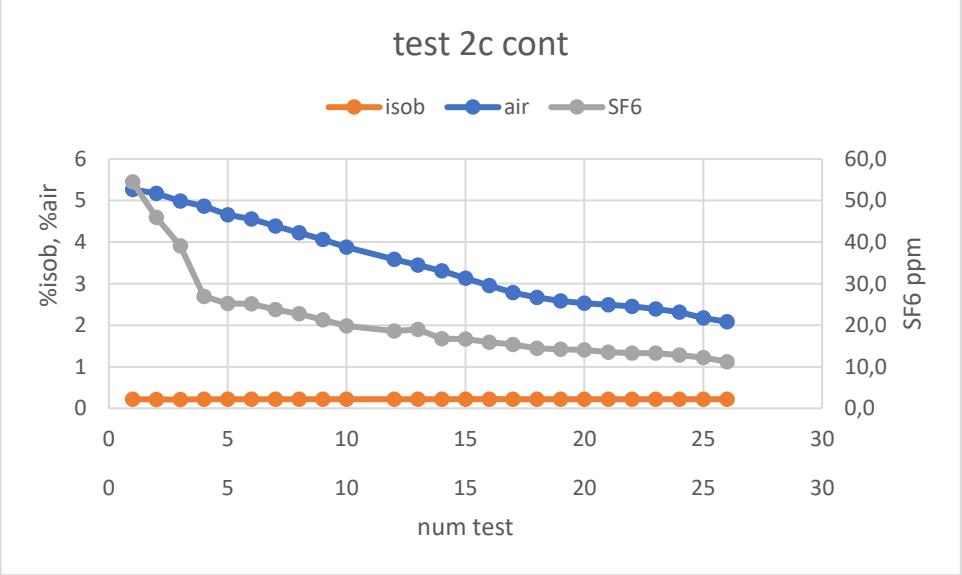

Figure 41 test 2c cont, input flow 200 l/h with compressor

The concentration trends are the same also in the other test performed in the same condition. The presence of SF_6 and the high concentration of air could be caused by the high speed velocity of the transfer between buffer 2 and buffer 1, and because the buffer 2 is not completely filled; as consequence because the boiling of the mixture caused by the compressor part of the vapor phase in equilibrium with the liquid phase is sent to the buffer 1 (the presence of SF_6 confirm this hypothesis because it is only in the vapor phase and it does not become liquid at the working temperature).

The isobutane's concentration is higher than the test performed without the compressor because the same reason of the presence of SF_6, and paraphs because the increased flow velocity between the two buffers. In fact, it is visible a general trend that increasing the input flow (figure 43) and so the velocity flow between buffers 2 and 1, increase the concentration of isobutane

3.1) we have tried to avoid that the compressor sent to the buffer 1 also a part of the vapor phase keeping the buffer 2 always full, because the liquid level that separate the vapor phase from the entrance of the connection tube between buffer 2 and 1 is higher than before. (table 9)

Table 9 last three tests in continuous result's list

Name	Input flow (l/h)	Isob (%)	Air(ppm)

4c cont	250	0,14	200
5c cont	300	0,21	300
6c cont	400	0,39	200

As shown in table 9 the concentration of air is back to normal values, and the SF_6 is no more present in the storage bottle. Maintaining Buffer 2 filled and with a constant level works to avoid sending also a part of the vapor phase to the buffer 1 and in the storage bottle.

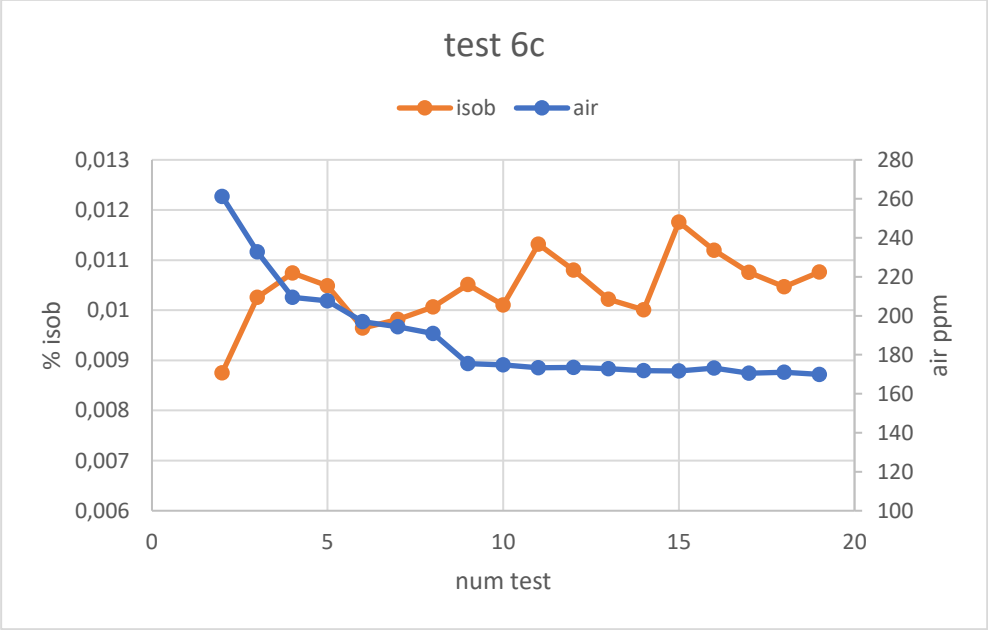

Figure 42 test 6c compressor, input flow 400l/h

Figure 42 shows that the concentration values of air and isobutane are constant during the analysis

The concentrations of isobutane are higher than the previous three analysis because also the input flow and the flow between the two buffers are increased.

The trend is once again that increasing the flow between the buffer 2 and buffer 1 increase the concentration of isobutane (figure 43)

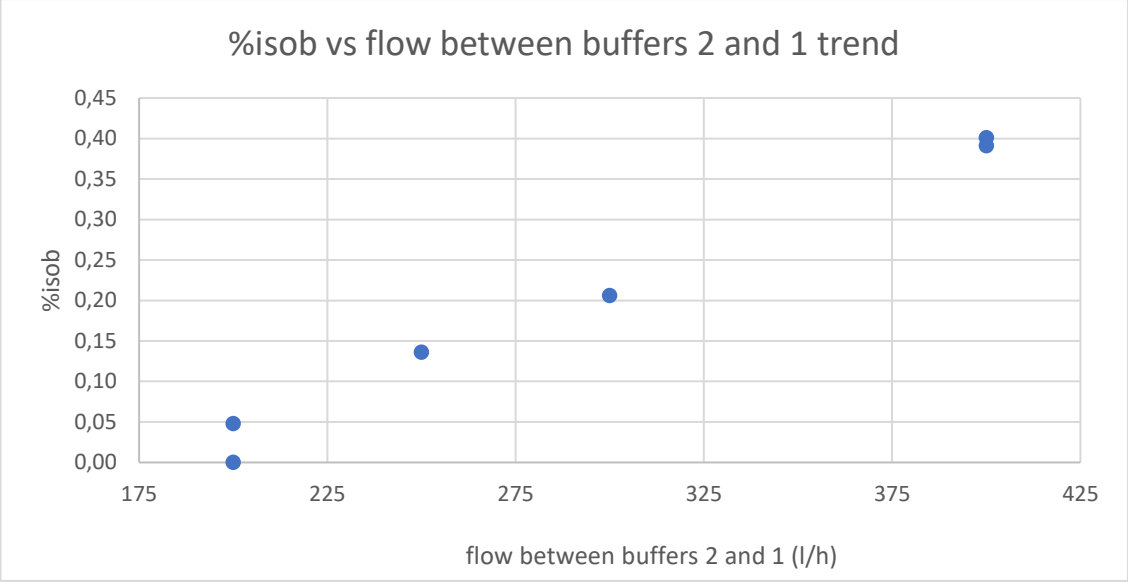

Figure 43 the visible trend is that higher the flow between buffers 2 and 1 higher the concentration of isobutane

This trend is caused by the fact that increasing the flow between buffers 2 and 1 decrease the time that the mixture spends in buffer 3 where the separation takes place, so a higher concentration of isobutane remains in the liquid phase and has no enough time to evaporate.

Part 4: in batch with compressor

Because of the failure with the continuous mode with the compressor the next step is to try to use the system in batch with the compressor to try to obtain good results in terms of concentration of isobutane and air.

4.0) initially we have not controlled any parameter controlled and especially the flow between buffers 2 and 1, to verify if the separation in this condition works or not (table 10)

Table 10 test list results part 4.0

Name	Flow buff 2-1 (l/h)	Isob(%)	Aria (ppm)
1c	400	0,03	300
2c	400	0,30	300
3c	400	0,41	100

As we can see from table 10 the concentration of air is pretty regular, while the concentration of isobutane varies a lot. The concentration variation of isobutane (especially between test 1c and the other 2 tests) could be caused by the different pressure difference between buffers 2 and 1 during the tests.

During test 1c the pressure in buffer 2 is 0 bar and also in buffer 1. The transfer speed of the mixtures between these two buffers is lower (comparable with the speed of the tests in part 1) than the transfer speed in other test where the pressure in buffer 1 was around -0,14mbar, while the pressure in buffer 2 was 0 bar.

From these preliminary tests we have noticed that the flow between the two parts of the system influence the performance of the separation.

4.1) We have tried to control the flow between the two parts of the system to verify this hypothesis.

Table 11 tests list in batch with compressor to verify the influence of the flow between the two parts of the system

Name	Flow buff 2-1 (l/h)	Iso(%)	Air (ppm)
4c	250	0,06	400
5c	150	0,02	100
6c	400	0,07	100
7c	400	0,25	500
8c	100	0,16	300

During the analysis in the single test the value of isobutane and air is stable. In figure 44 there is an example of the test 4c

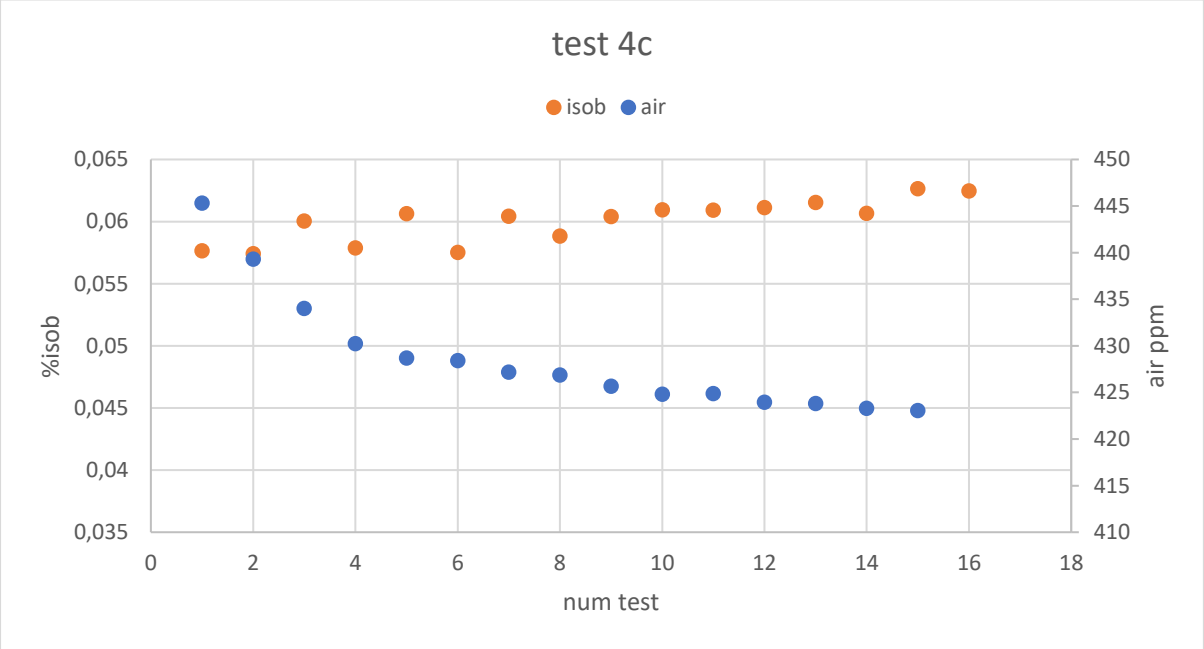

Figure 44 test 4c

Also, this time the concentration of the air is pretty stable in the various tests while the concentration of isobutane vary a lot. It is visible that increasing the flow between the two parts of the system increases the concentration of isobutane as in the tests made before.

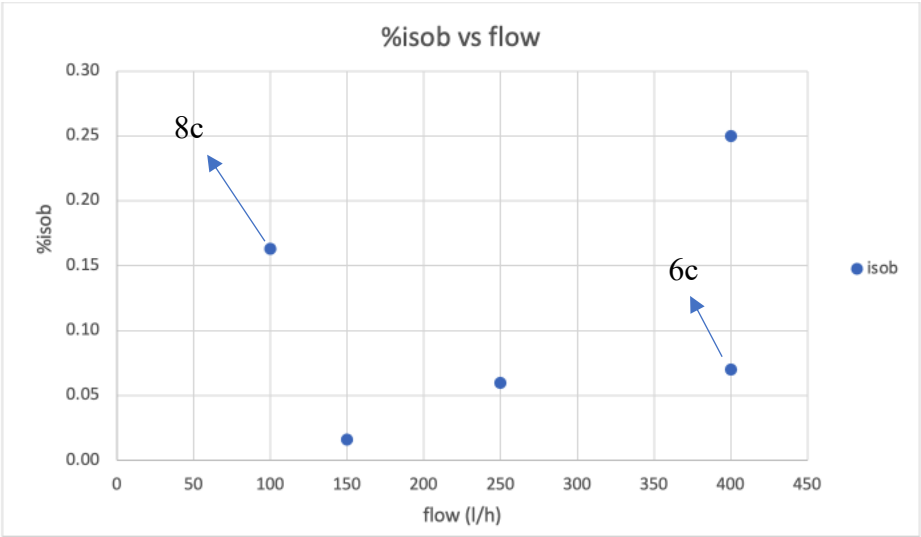

Figure 45 tests with the flow between the two part regulated, influence of the flow on the isobutane's concentration

In figure 45 and table 12 we can see that tests 6c and 8c do not follow the general trend. In the case of test 6c is because the mixture has waited an entire night in the buffer 2 before the analysis, so the separation has had enough time to take place.
Test 8c has a flux of 100 l/h but the isobutane's concentration is 0,16%; a higher concentration than test 4c and 5c that have a higher flux. A hypothesis for these results is that we have emptied the buffer 2 more than in the other tests (table 12)

Table 12 differential pressure in buffer 2 during the emptying

Name	Range P emptied (mbar)
4c	31,7- 14,5
5c	36- 14,1
6c	36-15,5
7c	36-18,2
8c	36-12,0

This could cause the fact that part of the vapor phase in equilibrium with the liquid phase is sent to the next buffer so the concentration of isobutane is higher, even if the concentration of SF_6 and air do not change from the other test; an hypothesis to justify this is that the flow was really small, so the SF_6 and air sent to the storage bottle are not enough to increase the total concentration.

4.2) In this subset of tests we have controlled not only the flow between the two parts of the system, but also the minimum liquid level inside buffer 2 to avoid that some part of the vapor phase was sent to the next buffer.

Table 13 tests in batch with compressor controlling the minimum liquid level inside buffer 2

Name	Flow buff 2-1 (l/h)	Range P emptied (mbar)	Isob (%)	Aria (ppm)
9c	400	36-20	0,15	300
10c	400	36-20	0,15	100
12c	150	36-22	0,02	100
13c	250	36-26	0,04	400
14c	400	36-24	0,11	100
15c	250	36-24	0,06	100
16c	150	36-20	0,00	100

The minimum level achieved is 20 mbar, and this could allow to obtain better results. As shown in table 13 the concentration of isobutane varies a lot again; but the higher results of this series of tests is smaller than the higher results of the previous test where the level of buffer 2 is no controlled and is also smaller than the test performed in continuous. The concentration of air however is always stable.

The general trend that we can see again is that increasing the flow between the two parts of the system increases the concentration of isobutane (figure 46).

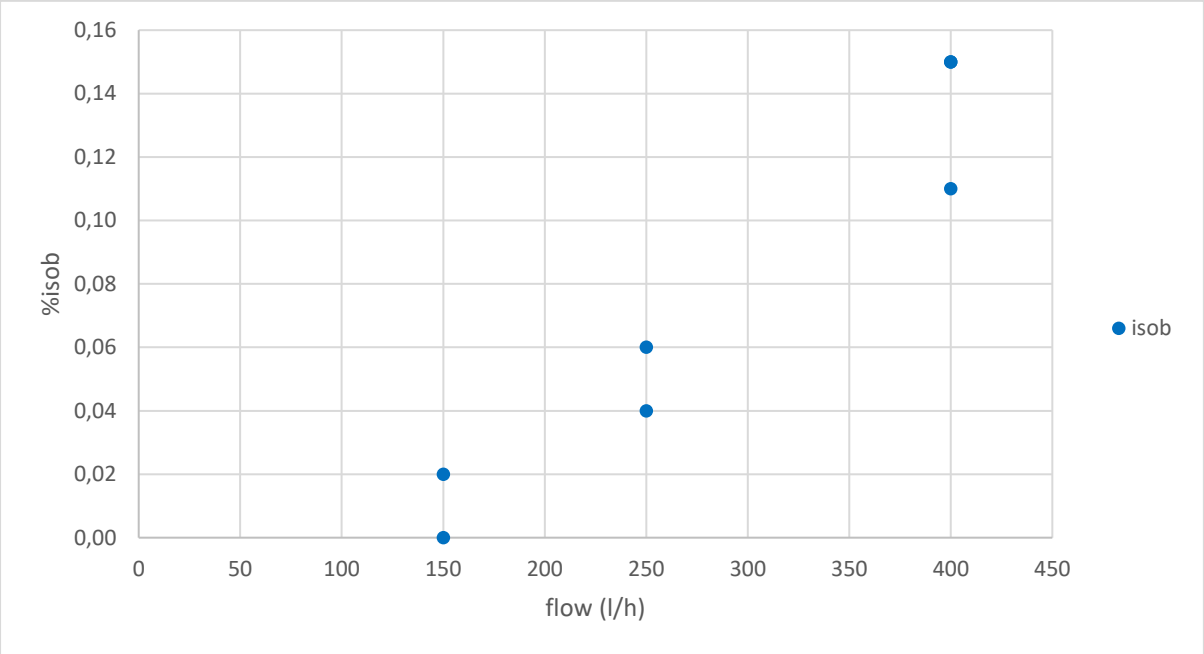

Figure 46 tests in batch with compressor controlling the liquid level in buffer 2 general trend respect the flow between the two parts of the system.

In test 16c we do not have isobutane at all; this is the first time that this result is achieved when the compressor is used. During this test the temperature of buffer 3 is unusually high (6,5°C) because of a failure of the gas room heating system.

The buffer 3 temperature, generally, is slightly lesser than the better temperature found in the previous work, when the compressor is working (table 14)

That could be caused by the fact that the flow between the two parts of the system is higher than it in the previous work, so a bigger volume of mixture passes through the buffer 3, causing the temperature decrease, and also the time that have the separation to take place is lesser. We have tried to increase this temperature over 4.5°C

4.3) To allow the separation takes place in the buffer 3 we have increased its bath temperature in a range between 9-10°C.

Table 14 test in batch with compressor related to the buffer's 3 temperature

Name	Flow buff 2-1 (l/h)	Isob (%)	Air (ppm)	T buff 3 (°C)
4c	250	0,06	400	3,69
5c	150	0,02	100	4,01
6c	400	0,07	100	3,37
7c	400	0,25	500	3,26
8c	100	0,16	300	3,26
9c	400	0,15	300	3,8
10c	400	0,15	100	3,8
12c	150	0,02	100	3,37
13c	250	0,04	400	4,66
14c	400	0,11	100	3,69
15c	250	0,06	100	3,8
16c	150	0,00	100	6,5
17c	400	0,02	100	9
18c	400	0,005	100	9,37
19c	400	0,01	300	9,37
20c	400	0,008	100	9,48

As we can see from table 14 the performance of the system increase if the temperature of the buffer 3 is higher than the temperature in the previous work. The efficiency is still ok also with this change in the condition of the system (table 15) and they are comparable to the efficiency of the previous part (tables 3 and 6) where the average efficiency was around 80%. Also, the efficiency obtained in the previous work was around 80% (Cambie, 2021). The efficiencies are calculated confronting the tola amount of gas injected in the system, with the increase in weight of the storage bottle.

Table 15efficiency of tests with T buff 3 increased

Name	V tot injected (l)	Weight increased (kg)	Efficiency (%)
18c	360	1,19	77,8
19c	425	1,42	78,6
20c	420	1,40	78,4

From this experiment we can see that the performances of the separation are influenced by the heat that the mixture can absorb when is in buffer 3. Increasing the flow between the two parts of the system, the temperature of buffer 3 decreases, so the heat is not enough to make the

separation at these speed. Increasing the temperature of buffer 3 allows to have more heat to exchange with the mixture, so even if the flow is higher the performance of the separation is still ok.

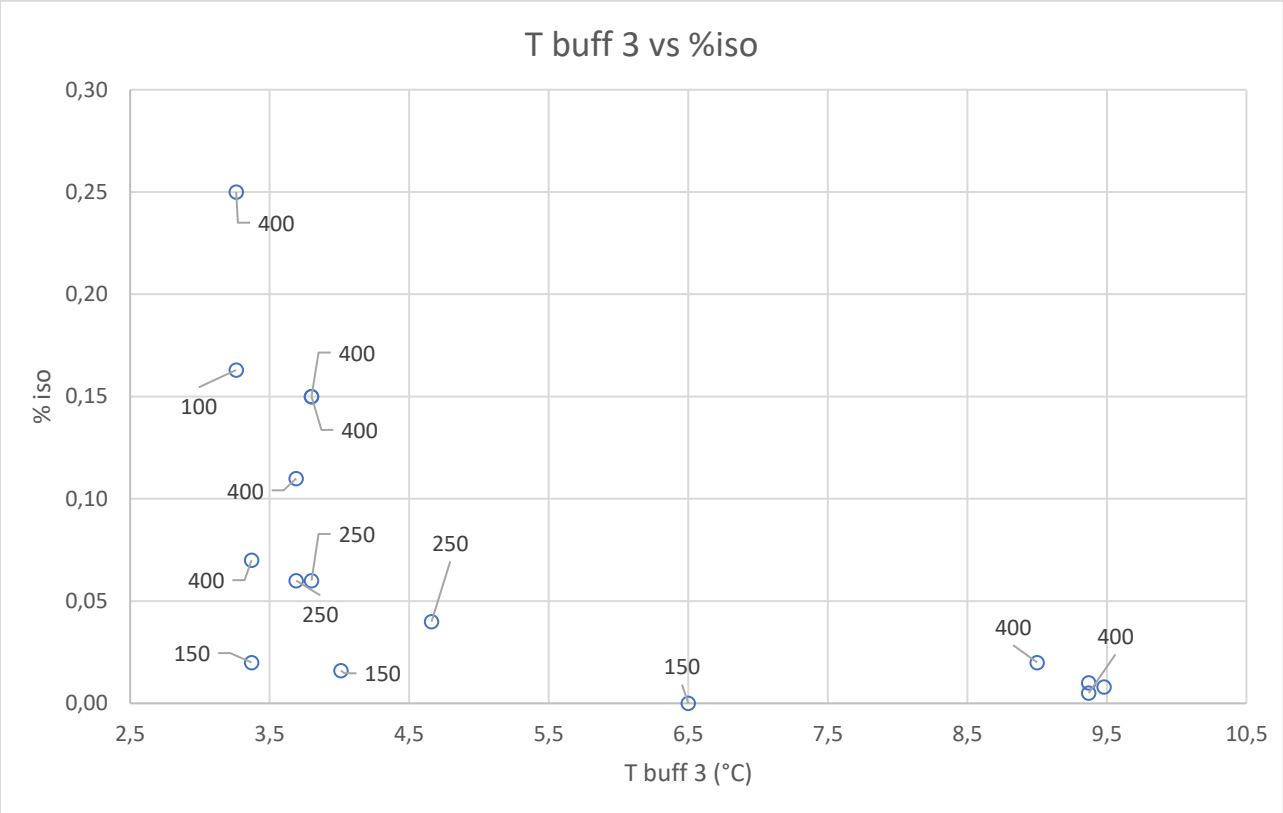

Figure 47 correlation between concentration of isobutane and buffer's 3 temperature of the tests from 4c to 20c. The number connected to any dots is the flow between the two part of the system expressed in l/h.

In figure 47 there is the correlation between the concentration of isobutane and the buffer's 3 temperature. In the temperature range between 2,5°C and 4,5°C the value of the isobutane concentration varies a lot also with the tests performed with the same flux between buffer 2 and 1. That is caused by all the other parameters that were tested in this work.

3.2) After test 20 we have tried to perform two other tests in continuous with the temperature of buffer 3 controlled to a higher value (table 16). Buffer 2 is full during the process and its level of filling is constant.

Table 16 part 3.2 tests list

Nome	Isob(%)	Aria (ppm)	T buff 3 (°C)
7c cont	0,06	300	9,36
8c cont	0,018	100	9,15

The separation takes place also in continuous mode when the temperature of buffer 3 is above 9°C. Also, the concentration of air is comparable to the concentration of the others tests. We have done only two tests in continuous because a problem with the compressor that limit its working time.

Conclusion

Dividing the experimental phase into different parts has permitted to study the parameters that influence the separation one by one and to find the better setting for all of them. The conclusions are that the heat that the bath of buffer 3 can exchange with the mixture (controlled with the temperature of the bath) and the time that the mixture waits in buffer 3 have primary importance to obtain better performance because they allow the separation to take place. These parameters are dependent to the flow between the two parts of the system and to the temperature of the bath of the buffer 3.

Decreasing the flow between the two parts of the system allow to the mixture to wait more time in buffer 3, so also if the temperature of the buffer 3 is $\geq$ 4,5°C the mixture have enough time to exchange heat with the bath of buffer 3 and so to the distillation to takes place.

Increasing the flow between the two parts of the system has the consequence that the mixture wait to less time in buffer 3 to exchange enough heat with the bath of buffer 3 (when the temperature of this bath is $\geq$ 4,5°C), so increasing the temperature of the bath it is possible to decrease the time needed to the mixture to receive enough heat and also higher flow between the two parts of the system are available to obtain the separation.

There are also others element that can influence the performance of the system, for example the time that the mixtures wait in buffer 2 (and so also in buffer 3) before the transfer to the buffer 1, in some occasion the fact that the mixture wait an entire nigh inside the buffer 2 (and so a part also in 3) allow to obtained better performance compared with other tests performed in the same condition but without the waiting time.

Because the goal of the system is to obtain the more possible quantity of R134a in the less time possible, the waiting time of the mixture in buffer 2 (and so a part in buffer 3) is no studied because this time in buffer 2 during its future normal work is 0.

Also, the minimum filled status of buffer 2 during the work of the system is important, if it is emptied to much some of the vapor phase is sent to the buffer 1 and so a higher concentration of isobutane will be in the storage bottle.

In figure 46 all this is visible. There is a test where the flow between the two parts of the system is 100 l/h (test 8c) but the concentration of isobutane is 0,16% because we emptied the buffer 2 too much. Other tests show how the concentration of isobutane is around 0,07% even if the

flow between the two parts of the system is 400 l/h (test 6c) because the mixture waits some time in buffer 2 before it was sent to the next buffer.

This is still a prototype; the new recuperation system must be constructed to work or in semicontinuous mode or in continuous mode.
Semicontinuous mode is like a batch mode but there is another first part of the system (buffer 2 and buffer 3) where the separation takes place, so alternating the two first part connected to the input flow we can have one of them that is filling and, in the meantime, the other of them is emptying in the next buffer. in this way we can use continuously also the system even if it does not work in continuous mode.
The continuous mode is possible to make but more tests are needed to verify is reliability.

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